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(71) Applicant: UNION CARBIDE CORPORATION
39 Old Ridgebury Road
Danbury Connecticut 06817(US)

(72) Inventor: Koleske, Joseph Victor
1513 Brentwood Road
Charleston 25314 West Virginia(US)
Inventor: Kwiatkowski, George Thomas
5 Forest Lane
Green Brook 08812 New Jersey(US)

(74) Representative: Freiherr von Pechmann, Eckehart et al
Patentanwälte Wuesthoff- v. Pechmann-Behrens-Goetz Schweigerstrasse 2
D-8000 München 90(DE)

(54) Photocurable blends of cyclic ethers and cycloaliphatic epoxides.

(57) Radiation-curable compositions comprising combinations of cycloaliphatic epoxides and cyclic ethers such as cycloaliphatic ethers cure rapidly when initiated by photoinitiators which form cationic catalysts when irradiated with e.g., ultraviolet light. The compositions can also contain other ingredients including poly(active hydrogen) compounds, vinyl ethers (linear and cyclic), glycidyl ethers, poly(vinyl halides), and polylactones. Radiation-cured coatings can be prepared from the compositions, using reduced quantities of the photoinitiator.

EP 0 262 414 A3

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EUROPEAN SEARCH REPORT

Application Number

EP 87 11 2575

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 123 912 (UNION CARBIDE CORP.) * Claims *	1	G 08 G 59/24 G 03 C 1/68 G 03 F 7/10 C 08 L 63/00
Y	EP-A-0 109 851 (3M) * Page 27, lines 23-25 *	1	
A	WO-A-8 501 947 (LOCTITE CORP.) * Page 7, line 8; page 8, lines 2-4; claims 1-4 *	1	
A	US-A-4 294 746 (E.B. BLAIR et al.)	1	
A	CHEMICAL ABSTRACTS, vol. 91, no. 4, 23rd July 1979, page 5, abstract no. 21201k, Columbus, Ohio, US; J.V. CRIVELLO et al.: "Photoinitiated cationic polymerization with triarylsulfonium salts", & J. POLYM. SCI., POLYM. CHEM. ED. 1979, 17(4), 977-999 * Abstract *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 08 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02-06-1989	VON KUZENKO M.T.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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EP 0 262 414 A2

PHOTOCURABLE BLENDS OF CYCLIC ETHERS AND CYCLOALIPHATIC EPOXIDES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This application pertains generally to radiation curable and photocurable compositions. More specifically, this application pertains to compositions which are curable with ultraviolet light, using photoinitiators which form cationic catalysts.

2. Description of the Prior Art

It is well known that coatings play a useful role in the manufacture of a wide variety of useful articles. Until recently, nearly all coatings were formulated and applied by employment of an organic solvent, which often comprised a major portion of the total formulated coating. After the coating is applied to the article to be coated, the organic solvent is evaporated, leaving the dried coating on the article to serve its decorative or functional purpose. This coating system has met with increasing disfavor as the cost of energy needed to evaporate the solvent at the rate required by industry increased, as the price of the solvent increased, and as the deleterious environmental effects of the evaporated solvent became better understood. In addition, governmental regulations have placed ever increasing restrictions on the amounts and types of solvents or organic volatiles permitted to escape into the atmosphere from coatings' compositions. Systems aimed at solvent recovery to reduce pollution and conserve solvent have generally proven to be energy intensive and expensive.

Considerable efforts have been expended by those skilled in the art to develop coating compositions having a minimal amount of volatile organic components and this has led to development of powder coatings, radiation-curable coatings, water-borne coatings and high solids coatings. In these recent developments, the amounts of organic solvents present are minimal and consequently there is little or no atmospheric pollution.

Among the new coating systems, radiation-curable coatings, usually cured with ultraviolet light or electron beam radiation, offer a variety of advantages. They require only minimal energy to effect cure (change from liquid to solid state), they do not contain volatile solvents, and thus do not cause deleterious effects to the environment, and they are cost effective, since essentially all of the applied liquid is converted to a solid coating.

An important disadvantage of photocurable systems is the frequent requirement that the curing process be conducted in an inert atmosphere because of the inhibiting effect of oxygen. Also, most photocurable systems based on acrylates are irritating to the skin and eyes of workers using them and can cause sensitization of those who are exposed to the systems.

Responding to such problems, those skilled in the art have devised photocurable coatings which cure through a mechanism termed cationic polymerization. In these systems, the starting materials are mixed with catalysts which form acids when exposed to ultraviolet light; the starting materials are therefore polymerized via cationic catalysis.

Epoxy resins, linear vinyl ethers, and cyclic vinyl ethers have been shown to be suitable starting materials for photocure via cationic polymerization, as disclosed in for example, U.S. -A-3,794,576; the publication of Crivello et al., "New Monomers for Cationic UV-Curing", Conference Proceedings, Radiation Curing VI, pages 4-28, September 20-23, 1982 (Association for Finishing Processes of SME): and GB-2,073,760A.

Crivello et al. reported that diaryliodonium and triarylsulfoniam salts could be used in relatively low concentrations as photoinitiators for UV curable coatings based upon multifunctional linear vinyl ether monomers. The cationic copolymerization of such vinyl ethers with epoxy monomers is also reported.

Although mixtures of cycloaliphatic epoxides and cyclic vinyl ethers are considered to be rapid curing in nature, with curing line speeds of 30 to 60 feet/minute readily attainable when a single light source is used, even further increases in curing speed are desirable to provide more productive, efficient and cost-effective industrial coating processes.

In contrast to the cyclic vinyl ethers and cyclic epoxides, cycloaliphatic ethers have been reported as slow in polymerizing under cationic photocuring conditions. See, e.g., Crivello and Lam, "Photoinitiator Cationic Polymerization by Diarylchloronium and Diarylbromonium Salts," Journal of Polymer Science, Polymer Letters Edition, Vol. 16, pp. 563-571 (1978), in which the polymerization of tetrahydrofuran when exposed to ultraviolet light in the presence of a photoinitiator was reported as very slow, particularly in contrast to the polymerization of the epoxide cyclohexene oxide.

Similarly, the applicants have observed that when a substituted cycloaliphatic ether such as 2-methoxytetrahydropyran alone is combined with an onium salt photoinitiator and exposed to ultraviolet light, only slow polymerization takes place.

SUMMARY OF THE INVENTION

Surprisingsly, it has been discovered that when a cycloaliphatic ether is added to a composition comprising a cycloaliphatic epoxide which is suitable for photopolymerization, the rate of curing in the presence of ultraviolet light and a photoinitiator which produces a cationic catalyst is increased by at least an order of magnitude compared to that of a similar composition without the added cycloaliphatic ether.

It has further been discovered that such enhanced reaction rates can be produced with reduced amounts of the photoinitiator, producing cost savings of commercial significance due to reduced consumption of the relatively expensive compounds customarily used.

In accordance with the present invention, a composition suitable for photopolymerization is provided which comprises at least one cyclic ether-containing compound and at least one cycloaliphatic epoxide containing at least one epoxy group, wherein the cyclic ether and the epoxy group(s) are contained in the same or different molecules. The cyclic ether can be cycloaliphatic, including oxacycloalkanes and oxacycloolefins, and preferably contains at least one substituent selected from the group consisting of alkyl, alkoxy, hydroxyalkyl, vinyl, substituted and unsubstituted aryl, nitro, sulfonyl, hydroxyalkyl groups reacted with oxyalkylene adducts, carboxylic acids or lactones, and halide groups. Most preferably, when substitutents are present, at least one substitutent is located adjacent to the ether linkage of the cycloaliphatic ether. Completely saturated cyclic ethers or oxacycloalkanes (free of cyclic ethylenic unsaturation) are particularly preferred.

In another embodiment of the present invention, the photopolymerizable composition includes at least one additional ingredient selected from poly (active hydrogen) organic compounds (such as, for example, a polyol), cyclic and linear vinyl ethers, glycidyl ethers, poly(vinyl halides) such as poly(vinyl chlorides), poly(vinyl esters) such as poly(vinyl acetates), polylactones such as polycaprolactones, aryl-alkyl alcohol copolymers such as styrene-allyl alcohol copolymer; cellulosic polymers such as cellulose acetate, cellulose acetate butyrate, ethyl cellulose and the like and copolymers of vinyl halides and vinyl esters, glycidyl acrylates, hydroxyalkyl acrylates, and mixtures of such monomers.

In a preferred embodiment, the photopolymerizable composition also contains a photoinitiator which forms a cationic catalyst when irradiated in solution, preferably selected from the group consisting of diazonium salts, onium salts, and mixtures thereof.

Further, in accordance with the present invention, processes are provided for photopolymerizing the claimed compositions, preferably using a reduced amount of photoinitiator which is effective to produce a cure rate greater than that of a composition not containing the cyclic ether-containing compound.

Still further in accordance with the present invention, radiation-cured coatings are provided which are prepared in accordance with the claimed processes and from the claimed photopolymerizable compositions.

DETAILED DESCRIPTION OF THE INVENTION

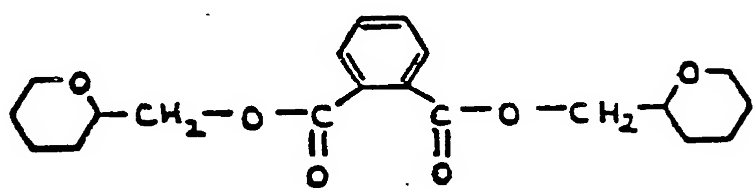
The addition of cyclic ethers to photocurable compositions containing at least one cycloaliphatic epoxide has been found to result in photopolymerizable compositions which provide greatly increased cure rates even with the use of reduced amounts of photoinitiator.

Although the compositions in the examples of the present application have been cured by exposure to ultraviolet light, the improvements of the present invention can be obtained in systems which are cured by any type of electromagnetic radiation of a suitable energy level, provided an appropriate photoinitiator is present. Effective sources of radiation include, but are not limited to, gamma rays, X-rays, electron beams, ultraviolet light, and visible light. Thus, although the terms "photocuring", "photopolymerization" and the like

are used in the present application with reference to work done with ultraviolet light, they should be considered equivalent to radiation curing or polymerization in a general sense. The terms "photocopolymerizable" and "photocopolymerize" indicate that at least some of the components of the composition (the cycloaliphatic epoxide, optional monomers or polymeric components, and the cyclic ether) copolymerize when irradiated in the presence of a photoinitiator. While some components may be homopolymerized to some degree, it is presently believed that at least some copolymerization takes place, and it is presently preferred that copolymerization predominates, as the crosslinking provides more desirable properties in the cured coating.

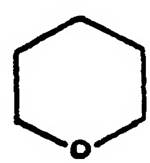
The compositions of the present invention contain the cycloaliphatic epoxides as described below, optionally in combination with other monomers and polymeric components, and the cyclic ethers as described below. The photoinitiator can be added in the desired quantity at the time the composition is to be cured, or alternatively, can be included as part of the composition. It has been found that compositions of the present invention are surprisingly stable even when the photoinitiator is included, producing equivalent curing results after a year's storage.

The cyclic ether-containing compounds useful in the present invention comprise cyclic ethers alone as well as such ethers included in more complex ring structures, such as polycyclic or fused ring structures, polymeric structures or complex molecules. For example, a biscyclic ether can be prepared by coupling or condensing two molecules of a hydroxyalkyl cyclic ether with a dicarboxylic acid or anhydride such as phthalic anhydride to produce a structure such as shown in the formula below:



As apparent to those skilled in the art, the nature and size of the structure connecting the ether rings can be varied by choosing from various diacids capable of esterifying the hydroxyalkyl group, and using hydroxyalkyl substituents having from 1 to 10 carbon atoms, for example. The cyclic ether structure itself can be saturated or unsaturated, substituted or unsubstituted, and preferably can have from 4 to 10 ring carbon atoms. Although cyclic ethers which are part of more complex structures can be more effective in causing gelling or polymerization of the compositions during curing, presently it is preferred to use simple cyclic ethers due to commercial availability and the excellent results obtainable. The cyclic ether and other components should combine to produce a composition having a viscosity suitable for application as a coating or other desired product, but no component should be so volatile as to cause significant loss of ingredients from the composition during the preparation, shipment, storage, application or curing stages.

Preferably the cyclic ether structure contains from 4 to 6 ring carbon atoms, and most preferably includes the 5-carbon pyran ring structure.

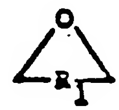


The cyclic ethers can be saturated or unsaturated, e.g., containing at least one double bond adjacent to the ether linkage to form what are referred to as cyclic vinyl ethers. Suitable cyclic vinyl ethers include dihydropyranyl and di-(dihydropyranyl) compounds.

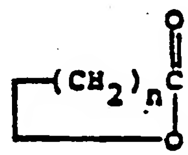
Cyclic ethers with double bonds further removed from the ether linkage can also be used. The completely saturated cyclic ethers are presently preferred, particularly those including the tetrahydropyran ring, as higher cure rates of the compositions are obtained with equivalent amounts of photoinitiators.

The cyclic ethers can be either unsubstituted or substituted, but the presence of substituents has been found to provide improvements, such as lower volatility of the ether and faster cure rates. The substituents when present are preferably electron-withdrawing groups such as alkoxy, hydroxyalkyl, halide, nitro, vinyl substituted and unsubstituted aryl, sulfonyl and halide. Alkyl, aryl, vinyl alkoxy, and hydroxyalkyl groups

having from 1 to 10 carbon atoms can be used. Preferably, these groups contain from 1 to 4 carbon atoms, and the methoxy group has been found to produce higher cure rates than groups with higher numbers of carbon atoms or hydroxyalkyl groups. Examples of suitable substituents in these categories include methyl, ethyl, and propyl groups, phenyl and phenyl substituted with halides or alkyl groups having 1-3 carbons. Alkaryl and aralkyl groups having from 7 to 12 carbon atoms can also be used. Other substituents which can be used include hydroxyalkyl groups -R-OH reacted with oxyalkylene adducts



such as ethylene or propylene oxide, to form a substituent containing an ether linkage $-R(-O-R_1)_mOH$, where $m = 1$ to 10, hydroxyalkyl groups reacted with substituted or unsubstituted lactones



(with $n = 4$-8) to form substituent groups containing an oxyester linkage

$$-R\left[O-\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_p\right]OH,$$

with $p = 1$ to 10, and hydroxyalkyl groups reacted with an organic carboxylic acid R_2COOH to form substituent groups containing an ester linkage,

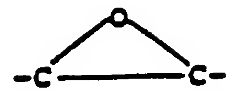
$$-R-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2.$$

The substituents can be present in any position on the ether ring, but preferably at least one substituent occupies a carbon atom adjacent to the ether linkage. When unsaturation is present, at least one substituent is preferably separated from the double bond(s) by at least one C-C bond.

Of the tetrahydropyran compounds used in the examples of the present application, 2-methoxy-tetrahydropyran is presently preferred due to the high cure rates obtained in comparison with 2-hydroxymethyltetrahydropyran and unsubstituted tetrahydropyran.

The cyclic ethers described above can be used in any suitable proportion of the total composition which will produce the desired cure rate and properties in the finished coatings or other cured products. Generally, the cyclic ether should constitute from 5 to 60 weight percent of the entire composition, preferably from 10 to 50 weight percent, and most preferably from 10 to 35 weight percent. the cyclic ether can also be blended in proportion to the amount of the cycloaliphatic epoxide present so that it is generally present as from 5 to 70 weight percent, preferably from 10 to 50, and most preferably from 15 to 45 of the combined weights of the cyclic ether and cycloaliphatic epoxide.

The compositions of the present invention in which the cure rate is increased by the presence of the cyclic ethers described above include an epoxide. The epoxides which may be used herein contain at least one epoxy group having the formula:

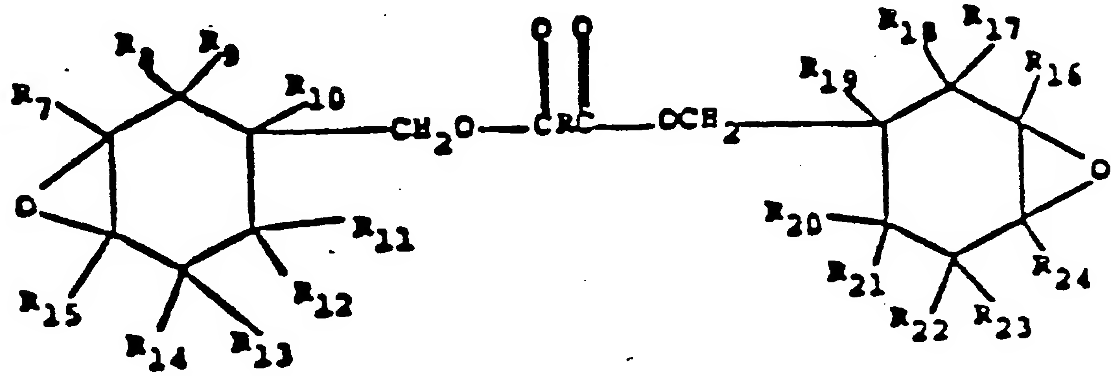


The epoxy groups can be terminal epoxy groups or internal epoxy groups. The epoxides are primarily cycloaliphatic epoxides, such as the compounds prepared by epoxidation of multicycloalkenyls (polycyclic aliphatic compounds containing carbon-carbon double bonds) with organic peracids (such as peracetic acid) or hydrogen peroxide. These cycloaliphatic epoxide resins may be blended with minor amounts of glycidyl type epoxides, aliphatic epoxides, epoxy cresol novolac resins, epoxy phenol novolac resins, polynuclear phenol-glycidyl ether-derived resins, aromatic and heterocyclic glycidyl amine resins, hydantoin epoxy resins, epoxides of natural oils such as soybean and linseed oils, and mixtures thereof.

Preferred cycloaliphatic epoxide resins for purposes of this invention are those having an average of two or more epoxy groups per molecule. Illustrative of suitable cycloaliphatic epoxides are the following:

FORMULA 1

Diepoxides of cycloaliphatic esters of dicarboxylic acids having the formula:



wherein R_7 through R_{24} can be the same or different, are hydrogen or alkyl radicals generally containing 1 to 9 carbon atoms, and preferably containing 1 to 3 carbon atoms as for example methyl, ethyl, n-propyl, n-butyl, n-hexyl, 2-ethylhexyl, n-octyl, and n-nonyl; R is a valence bond or a divalent hydrocarbon radical generally containing 1 to 20 carbon atoms, and preferably containing 4 to 6 carbon atoms, as for example, alkylene radicals, such as trimethylene, tetramethylene, pentamethylene, hexamethylene, 2-ethylhexamethylene, octamethylene, nonamethylene, and hexadecamethylene; cycloaliphatic radicals, such as 1,4-cyclohexane, 1,3-cyclohexane, and 1,2-cyclohexane.

Preferably the majority of R_7 to R_{24} are hydrogen. Particularly desirable epoxides, falling within the scope of Formula 1, are those wherein R_7 to R_{24} are all hydrogen and R is alkylene containing 4 to 6 carbon atoms.

Among specific diepoxides of cycloaliphatic esters of dicarboxylic acids are the following:

bis(3,4-epoxycyclohexylmethyl) oxalate,

bis(3,4-epoxycyclohexylmethyl) adipate,

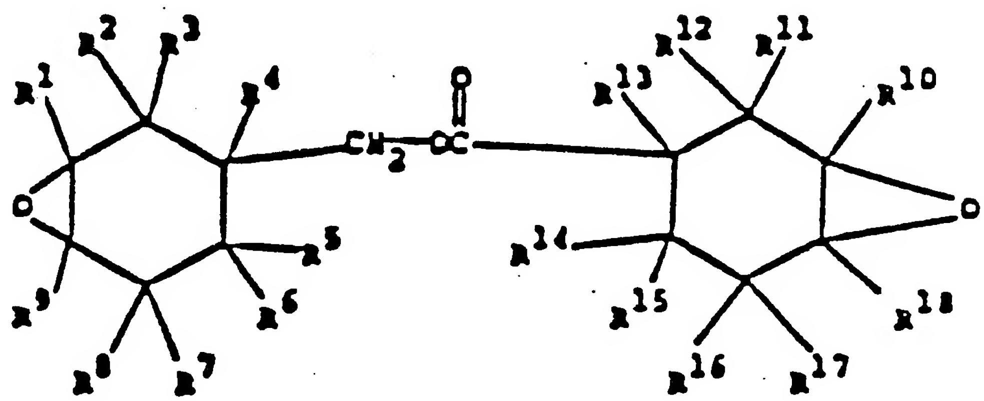
bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate,

bis(3,4-epoxycyclohexylmethyl) pimelate.

Other suitable compounds are described in, for example, U.S. -A-2,750,395.

FORMULA 2

A 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate having the formula:

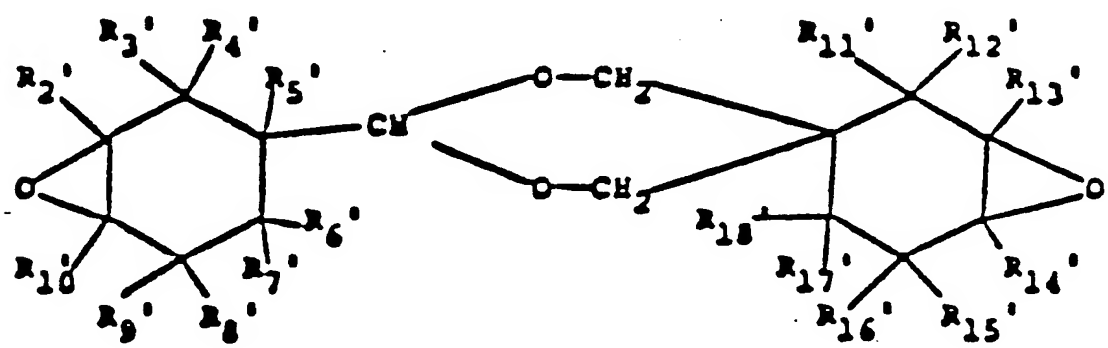


wherein R^1 to R^{18}, which can be the same or different, are as defined for R_7 to R_{24} in Formula 1. Preferably the majority of R^1 to R^{18} are hydrogen. Particularly desirable compounds are those wherein R^1 to R^{18} are hydrogen.

Among specific compounds falling within the scope of Formula 2 are the following: 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate; 3,4-epoxy-1-methylcyclohexylmethyl-3,4-epoxy-1-methycyclohexane carboxylate; 6-methyl-3,4-epoxycyclohexylmethyl-6-methyl-3,4-epoxycyclohexane carboxylate; 3,4-epoxy-3-methylcyclohexylmethyl-3,4-epoxy-3-methylcyclohexane carboxylate; 3,4-epoxy-5-methylcyclohexylmethyl-3,4-epoxy-5-methylcylcohexane carboxylate. Other suitable compounds are described in, for example, U.S. -A-2,890,194.

FORMULA 3

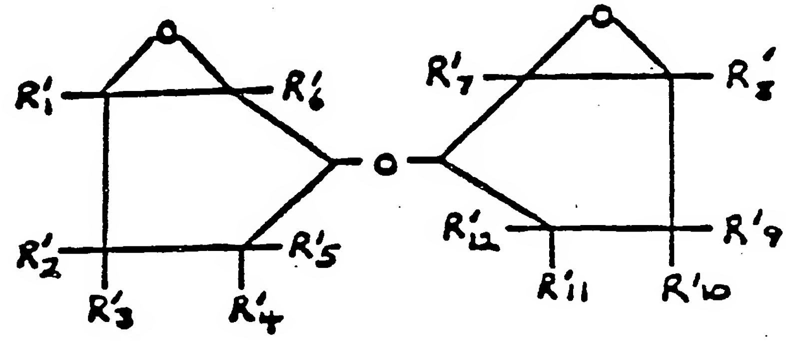
Diepoxides having the formula:



wherein the R's, which can be the same or different, are monovalent substituents such as hydrogen, halogen, i.e., chlorine, bromine, iodine or fluorine, or monovalent hydrocarbon radicals, or radicals as further defined in U.S.-A-3,318,822. Preferably a majority of the R's are hydrogen. Particularly desirable compounds are those wherein all the R's are hydrogen.

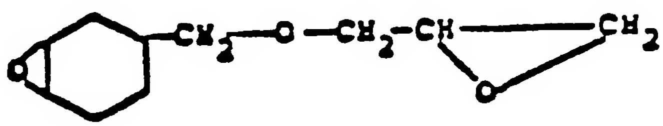
FORMULA 4

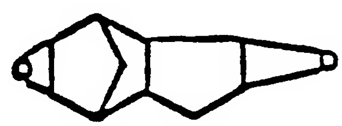
Preferred cycloaliphatic diepoxides are those in the family of bis(2,3-epoxycyclopentyl) ethers having the formula:

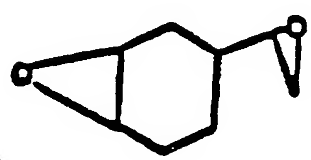


wherein the R's, which can be the same or different, are monovalent substituents such as hydrogen, halide, i.e., chlorine, bromine, iodine or fluorine atoms, or monovalent hydrocarbon radicals. Preferably a majority of the R's are hydrogen. Particularly desirable compounds are those wherein all the R's are hydrogen.

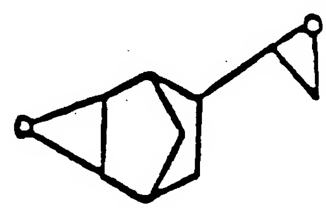
Other suitable cycloaliphatic epoxides include the following:

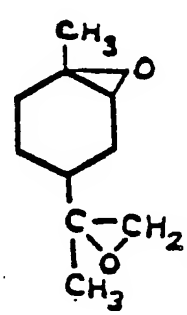




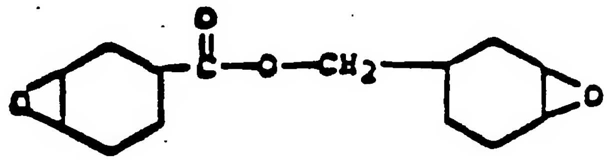


or

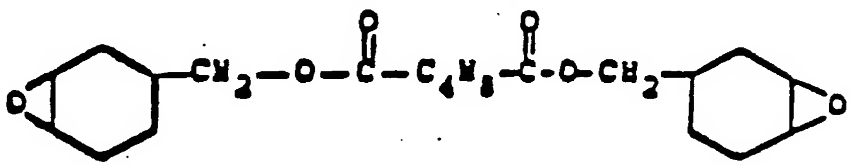




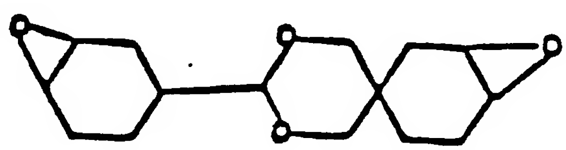
Some presently preferred cycloaliphatic epoxides are the following:
3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate,

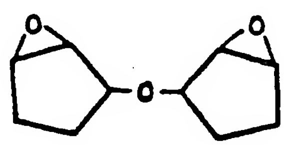


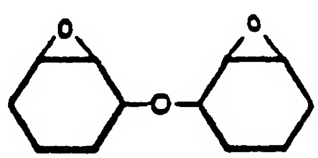
Bis(3,4-Epoxycyclohexylmethyl)adipate, and



2-(3,4-Epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-meta-dioxane,

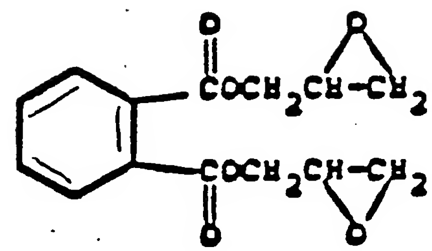






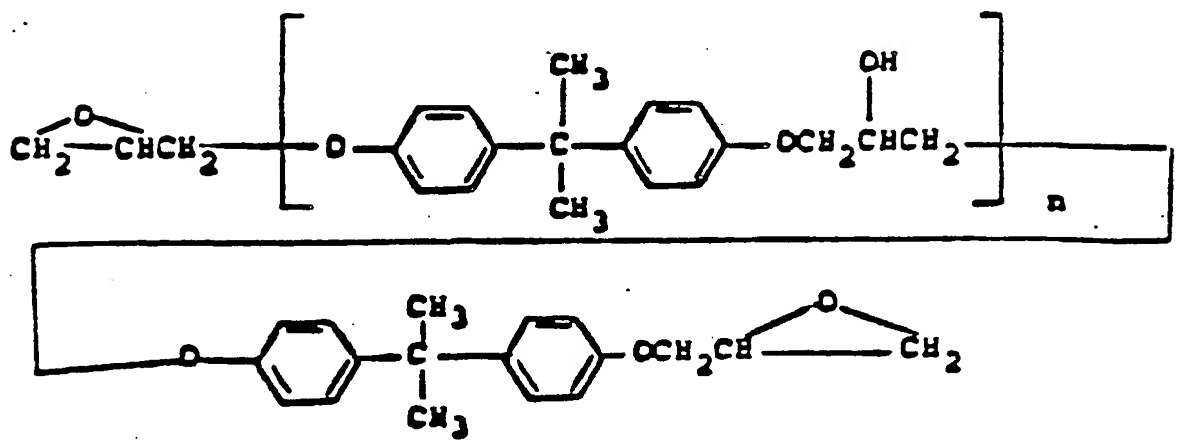
or mixtures thereof.

Epoxides with 6-membered ring structures can also be used, such as diglycidyl esters of organic diacids such as phthalic acid, partially hydrogenated phthalic acid or fully hydrogenated phthalic acid. A representative diglycidyl ester of phthalic acid is the following:



Diglycidyl esters of hexahydrophthalic acids are preferred.

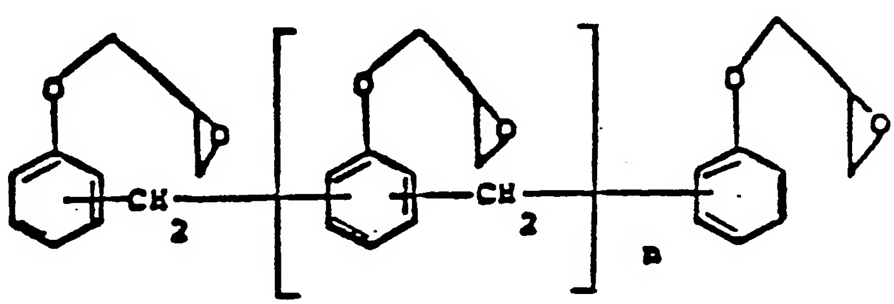
The glycidyl-type epoxides are preferably diglycidyl ethers of bisphenol A which are derived from bisphenol A and epichlorohydrin and have the following formula:



Also included are partially or fully hydrogenated compounds of the above general structure.

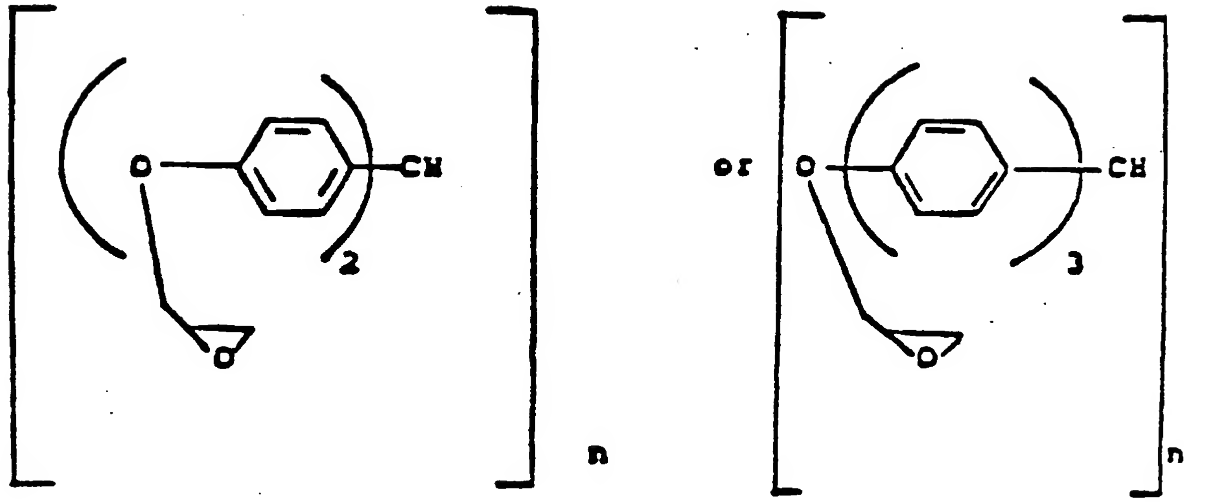
The cresol-novolac epoxy resins are multifunctional, solid polymers characterized by low ionic and hydrolyzable chlorine impurities, high chemical resistance, and thermal performance.

The epoxy phenol novolac resins are generally of the following formula:

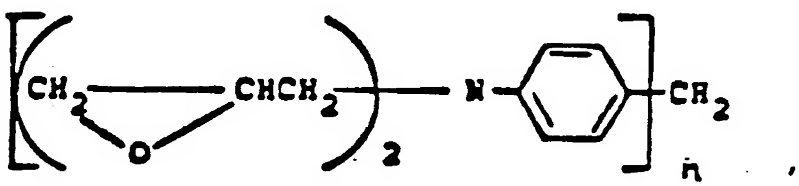


Also included are partially or fully hydrogenated compounds of the above general structure.

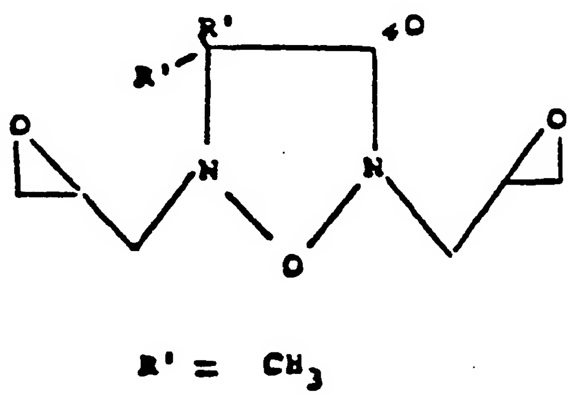
The polynuclear phenol-glycidyl ether-derived resins are generally of the formula:



Among the aromatic and heterocyclic glycidyl amine resins which may be included herein are the following: tetraglycidylmethylenedianiline derived resins of the following formula:



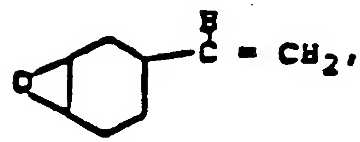
and
triglycidyl-p-aminophenol derived resins, triazine based resins and hydantoin epoxy resins of the formula:



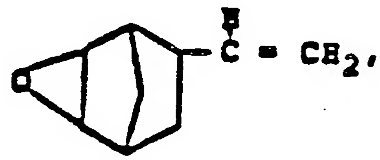
It is of course understood by those skilled in the art that when a photoinitiator is used only minor amounts of basic organic nitrogen containing epoxide compounds may be used so as not to interfere with the photocopolymerization reaction.

Although the diepoxides described above are presently preferred, the composition can include a substituted or unsubstituted cycloaliphatic monoepoxide. The unsubstituted cycloaliphatic monoepoxides include cyclohexene monoepoxide. The substituted cycloaliphatic monoepoxide can be substituted with alkyl groups of 1 to 9 carbon atoms, halogen, oxygen, ether, ester, hydroxyl or vinyl radicals. Preferably, the substituted cycloaliphatic monoepoxide is a vinyl substituted cycloaliphatic monoepoxide and is preferably selected from one or more of the following:

(1) 4-vinyl cyclohexane monoepoxide having the formula:

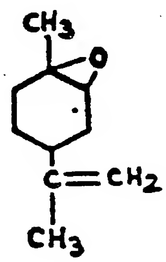


(2) Norbornene monoepoxide having the formula:

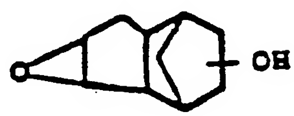


or

(3) limonene monoepoxide having the formula:



Another preferred substituted cycloaliphatic monoepoxide is hydroxyl substituted cycloaliphatic monoepoxide of the following formula:

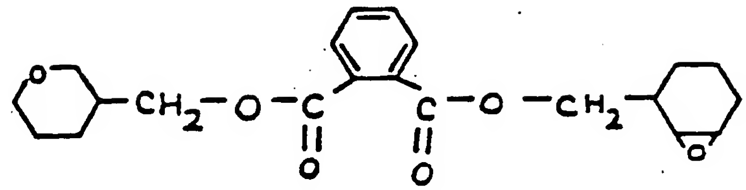


Epoxides having more than 2 epoxide groups are also useful in the present invention, and may have particular utility when very high cure rates or very low photoinitiator concentrations are employed.

In an embodiment, the cycloaliphatic epoxide and cyclic ether described above can be combined in a single molecule, ranging from complex polycyclic fused rings or bicyclic structures to single ring structures, e.g., epoxidized cyclic ethers. Various synthetic routes known to those skilled in the art can be employed to produce molecular structures containing at least one cyclic ether linkage selected from those described above and at least one epoxy group, preferably contained in a structure selected from those described above.

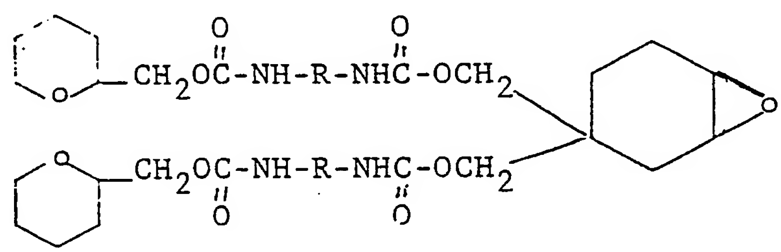
As apparent to those skilled in the art, such bifunctional molecules can be cured by cationic polymerization without the necessity of adding other cycloaliphatic epoxides or cyclic ethers, although it may be advantageous to use them in curable compositions containing such cycloaliphatic epoxides and/or cyclic ethers.

one type of a bicyclic ether-epoxide structure, for instance, can be prepared by condensing or coupling a molecule of a hydroxyalkyl cyclic ether such as tetrahydropyran-3-methanol with a molecule of a hydroxyalkyl cycloalkene such as tetrahydrobenzyl alcohol (3-cyclohexene-1-methanol) with an organic diacid or anhydride such as phthalic anhydride, then epoxidizing the double bond in the condensed molecule to produce a molecule containing separate rings which contain at least one ether linkage and at least one epoxy group, as in the structure shown below:



As apparent to those skilled in the art, the nature and size of the structure connecting the rings with the epoxy and ether functions can be varied by choosing from various diacids capable of esterifying the hydroxyalkyl groups, and using hydroxy alkyl substituents having from 1 to 10 carbon atoms, for example.

A type of multifunctional compound containing the cyclic ether linkage and epoxide group, for instance, can be prepared by condensing or coupling two molecules of a hydroxyalkyl cyclic ether such as tetrahydropyran-2-methanol with one molecule of a dihydroxyalkyl cycloalkene such as 3-cyclohexene-1,1-dimethanol, using a compound such as a multifunctional isocyanate, then epoxidizing the double bond in a cycloalkene ring (e.g., the 3,4 position of the cyclohexene ring). The final molecule will contain one ring with an epoxy group and 2 rings with cyclic ether linkages, as shown in the formula below. the multifunctional isocyanate can be $R(NCO)_2$, where R is selected from alkyl groups having from 1 to 10 carbon atoms, aryl groups having from 6 to 10 carbon atoms, and cycloalkyl groups having from 6 to 10 carbon atoms. The compound resulting from such a condensation with a multifunctional isocyanate will be a dicyclic ether/monocycloaliphatic epoxide urethane compound.



The cyclic ether linkage and epoxide group can be combined in single ring structures such as epoxidized cyclic ethers having from 4 to 20 ring carbon atoms and represented by the formula below where the sum of a + b is about 15 and a is the same as or different from b. Such compounds can contain at least one ether linkage and at least one epoxy group, with the epoxy groups being separated from the ether linkage and from each other by at least one methylene group, i.e., $-O-CH_2-(CH_2)_a-CH=CH(CH_2)_bCH_2-$.

In conjunction with the cycloaliphatic epoxide, the composition of this invention can also include a poly-(active hydrogen) organic compound. These poly (active hydrogen) organic compounds include any compatible organic compounds containing two or more active hydrogen atoms per molecule. The poly-(active hydrogen) organic compounds are well known to those skilled in the art and include, for example, organic polyols and the like.

Substantially any of the organic polyols previously used in the art to make coating compositions can be used and are preferred as the poly(active hydrogen) organic compounds in this invention. Illustrative of the polyols useful in producing coating compositions in accordance with this invention are the polyether polyols such as polyhydroxyalkanes and polyoxyalkylene polyols, the acrylic and vinyl polyols, the polyester polyols, the polycaprolactone polyols, and other lactone polyols such as polyvalerolactone polyols, polymethylcaprolactone polyols, the polymer/polyols, Among the polyether polyols which can be employed are those selected from one more of the following classes of compositions, alone or in admixture, known to those skilled in the art:

(a) Alkylene oxide adducts of polyhydroxyalkanes;
(b) Alkylene oxide adducts of non-reducing sugars and sugar derivatives;
(c) Alkylene oxide adducts of phosphorous and polyphosphorous acids.
(d) Alkylene oxide adducts of polyphenols;
(e) The polyols from natural oils, such as castor oil.

Illustrative alkylene oxide adducts of polyhydroxyalkanes include, among others, the alkylene oxide adducts of ethylene glycol, propylene glycol, 1,3-dihydroxypropane, 1,3-dihydroxybutane, 1,4-dihydroxybutane, 1,4-, 1,5-, and 1,6-dihydroxyhexane, 1,2-, 1,3-, 1,4-, 1,6-, and 1,8-dihydroxyoctane, 1,10-dihydroxydecane, glycerol, 1,2,4-trihydroxybutane, 1,2,6-trihydroxyhexane, 1,1,1,-trimethylolethane, 1,1,1,-trimethylolpropane, pentaerythritol, polycaprolactone, xylitol, arabitol, sorbitol, and mannitol.

A preferred class of alkylene oxide adducts of polyhydroxyalkanes are the ethylene oxide, propylene oxide and butylene oxide, adducts of trihydroxyalkanes or mixtures thereof.

A further class of polyether polyols which can be employed are the alkylene oxide adducts of the non-reducing sugars, wherein the alkylene oxides have from 2 to 4 carbon atoms. Among the non-reducing sugars and sugar derivatives contemplated are sucrose, alkyl glycosides, such as methyl glucoside, ethyl glucoside, and the like, glycol glycosides, such as ethylene glycol glucoside, propylene glycol glucoside, glycerol glucoside, 1,2,6-hexanetriol glucoside, as well as the alkylene oxide adducts of the alkyl glycosides as set forth in U.S. -A-3,073,788.

The alkylene oxide adducts of phosphorous and polyphosphorous acids are another useful class of polyether polyols. Ethylene oxide, 1,2-epoxypropane, the epoxybutanes, and 3,-chloro-1,2-epoxypropane are preferred alkylene oxides. Phosphoric acid, phosphorous acid, and the polyphosphoric acids, such as, tripolyphosphoric acid, the polymetaphosphoric acids are desirable for use in this connection.

A still further useful class of polyether polyols is the polyphenols, and preferably the alkylene oxide adducts thereof wherein the alkylene oxides have from 2 to 4 carbon atoms. Among the polyphenols which are contemplated are, for example, bisphenol A, bisphenol F, condensation products of phenol and formaldehyde, the novolac resins, condensation products of various phenolic compounds and acrolein, the simplest member of this class being the 1,1,3-tris(hydroxyphenol) propanes; condensation products of various phenolic compounds and glyoxal, glutaraldehyde, and other dialdehydes, the simplest members of this class being the 1,1,2,2,-tetra bis(hydroxyphenol) ethanes.

The polyether polyols described hereinabove can have hydroxyl numbers which vary over a wide range. In general, the hydroxyl numbers of the above described polyols employed in this invention can range from 15, and lower, to about 900, and higher. The hydroxyl number is defined as the number of milligrams of potassium hydroxide required for the complete neutralization of the fully phthalated derivative prepared from 1 gram of polyol. The hydroxyl number can also be defined by the equation:

$$OH = \frac{56.1 \times 1000 \times f}{m.w.}$$

where, OH = hydroxyl number of the polyol;

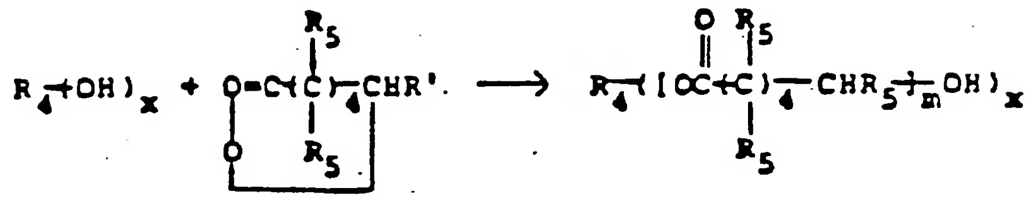
f = functionality, that is, average number of hydroxyl groups per molecule of polyol; and

m.w. = molecular weight of the polyol.

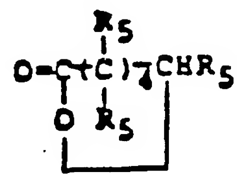
The polyether polyols described hereinabove can be prepared by conventional methods and are commercially available from a number of manufacturers.

The polycaprolactone polyols, alone or in admixture, that can be used to prepare the coating compositions of this invention include any of the known polycaprolactone polyols that are commercially available and that are fully described, for example, in U.S. -A-3,169,945. As described in this patent, the polycaprolactone polyols are produced by the catalytic polymerization of an excess of a caprolactone and an organic polyfunctional initiator having at least two reactive hydrogen atoms. The organic functional initiators can be any polyhydroxyl compound, as is shown in U.S. -A-3,169,945. Illustrative thereof are the diols, such as, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, dipropylene glycol, 1,3-propylene glycol, polyethylene glycol, polypropylene glycol, poly(oxyethylene-oxypropylene) glycols, and similar polyalkylene glycols, either blocked, capped or heteric, containing up to about 40 or more alkyleneoxy units in the molecule, 3-methyl-1-5-pentanediol, cyclohexanediol, 4,4'-methylene-bis-cyclohexanol, 4,4'-isopropylidene bis-cyclohexanol, xylenediol, 2-(4-hydroxymethylphenyl) ethanol, 1,4-butanediol, and 1,6-hexanediol; triols such as glycerol, trimethylolpropane, 1,2,6-hexanetriol, triethanolamine, and triisopropanolamine; tetrols, such as erythritol, pentaerythritol; and N,N,N',N'-tetrakis(2-hydroxyethyl) ethylene diamine.

When the organic functional initiator is reacted with the caprolactone, a reaction occurs that can be represented in its simplest form by the equation:



In this equation, the organic functional initiator is the R_4-$(OH)_x$ compound and the caprolactone is the



compound; this can be caprolactone itself or a substituted caprolactone wherein R_5 is hydrogen or an alkyl, alkoxy, aryl, cycloalkyl, alkaryl or aralkyl group having up to 12 carbon atoms and wherein at least 6 of the R_5 groups are hydrogen atoms, as shown in U.S. -A-3,169,945. In this expression, R_5 can be the same or different in each particular instance. The polycaprolactone polyols that are used are shown by the formula on the right hand side of the equation; they can have an average molecular weight of from 200 to 6,000. The preferred polycaprolactone polyol compounds are those having an average molecular weight of from 290 to 6,000, most preferably from 290 to 3,000. The most preferred are the polycaprolactone diol compounds having an average molecular weight of from 290 to 1,500 and the polycaprolactone triol and tetrol compounds having an average molecular weight of from 290 to 3,000; these are most preferred because of properties resulting from their low viscosity. In the formula, m is an integer representing the average number of repeating units needed to produce the compound having said molecular weights. The hydroxyl number of the polycaprolactone polyol can be from 15 to 600, preferably from 20 to 500; and the polycaprolactone can have an average of from 2 to 8, preferably 2 to 4, hydroxyl groups. Minor amounts of polycaprolactones having an average of approximately one hydroxyl group can also be employed.

Illustrative of polycaprolactone polyols that can be used in the coating compositions of this invention, one can mention the reaction products of a polyhydroxyl compound having an average from 2 to 6 hydroxy groups with caprolactone. The manner in which this type of polycaprolactone polyol is produced is shown in U.S. -A-3,169,945 and many such compositions are commercially available. In the following Table A, there are listed illustrative polycaprolactone polyols. The first column lists the organic initiator that is reacted with the caprolactone, and the average molecular weight of the polycaprolactone polyol is shown in the second column. Knowing the molecular weights of the initiator and of the polycaprolactone polyol, one can readily determine the average number of molecules of caprolactone (CPL Units) that reacted to produce the compounds; this figure is shown in the third column.

TABLE A

POLYCAPROLACTONE POLYOLS

Initiator molecules	Average MW of polyol	Average of CPL units in
1 Ethylene glycol	290	2
2 Ethylene glycol	803	6.5
3 Ethylene glycol	2,114	18
4 Propylene glycol	874	7
5 Octylene glycol	602	4
6 Decalene glycol	801	5.5
7 Diethylene glycol	527	3.7
8 Diethylene glycol	847	6.5
9 Diethylene glycol	1,246	10
10 Diethylene glycol	1,998	16.6
11 Diethylene glycol	3,526	30
12 Triethylene glycol	754	5.3
13 Polyethylene glycol (MW 200)[1]	713	4.5
14 Polyethylene glycol (MW 600)[1]	1,398	7
15 Polyethylene glycol (MW 1500)[1]	2,868	12
16 1,2-Propylene glycol	646	5
17 1,3-Propylene glycol	988	8
18 Dipropylene glycol	476	3
19 Polypropylene glycol (MW 425)[1]	835	3.6
20 Polypropylene glycol (MW 1000)[1]	1,684	6
21 Polypropylene glycol (MW 2000)[1]	2,456	4
22 Hexylene glycol	916	7
23 2-Ethyl-1,3-hexanediol	602	4
24 1,5-Pentanediol	446	3
25 1,4-Cyclohexanediol	629	4.5
26 1,3-Bis(hydroxyethyl)-benzene	736	5
27 Glycerol	548	4
28 1,2,6-Hexanetriol	476	3
29 Trimethylolpropane	590	4
30 Trimethylolpropane	750	5.4
31 Trimethylolpropane	1,103	8.5
32 Triethanolamine	890	6.5
33 Erythritol	920	7
34 Pentaerythritol	1,219	9.5
35 1,4-Butanediol	546	4.0
36 Neopentyl glycol	674	5.0

[1] Average molecular weight of glycol

The structures of the compounds in the above tabulation are obvious to one skilled in the art based on the information given. The structure of compound No. 7 is:

$$HO\left[(CH_2)_5\overset{O}{\overset{\|}{C}}O\right]_r CH_2CH_2OCH_2CH_2\left[O\overset{O}{\overset{\|}{C}}(CH_2)_5\right]_r OH$$

wherein the variable r is an integer, the sum of r + r has an average value of 3.7 and the average molecular weight is 527. The structure of compound No. 20 is:

$$HO\left[(CH_2)_5\overset{O}{\overset{\|}{C}}O\right]_r (C_3H_6O)_nC_3H_6\left[O\overset{O}{\overset{\|}{C}}(CH_2)_5\right]_r OH$$

wherein the sum of r + r has an average value of 6 and the average molecular weight is 1,684. This explanation makes explicit the structural formulas of compounds 1 to 34 set forth above.

Polycaprolactone hexols suitable for use in the present invention can be prepared by the catalytic polymerization of an excess of polycaprolactone polyols and a cycloaliphatic epoxide. Illustrative polycaprolactone polyols useful in the preparation of polycaprolactone hexols include polycaprolactone diols, and polycaprolactone triols, including mixtures thereof. Many of these polycaprolactone polyols are commercially available from Union Carbide Corp., Old Ridgebury Road, Danbury, CT 06817. Cycloaliphatic epoxides suitable for use in preparing the polycaprolactone hexols include 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis (3,4-epoxycyclohexylmethyl) adipate, and vinyl cyclohexane dioxide. Many of these cycloaliphatic epoxides are also commercially available from Union Carbide Corp. A suitable polymerization catalyst is diethylammonium triflate, which is commercially available from the 3M Company, Commercial Chemical Div., 2501 Hudson Road, St. Paul, MN 55119, as FC-520.

A preferred method for preparing the polycaprolactone hexols is comprised of adding one or more polycaprolactone triols to a reactor, heating the polycaprolactone triols to a temperature of about 100°C and adding the catalyst using a nitrogen sparge as soon as the polycaprolactone triols are molten. The polycaprolactone triols and catalyst mixture is then heated to a temperature of from 150°C to 200°C and a cycloaliphatic epoxide is added to the mixture. The reaction is carried out for 1 hour to 3 hours or until the oxirane content has been reduced to a nil or to an almost nil value. A modification of this process can involve initially adding all of the ingredients into the reactor. A further modification of this method can involve a vacuum treatment of from 10 to 30 minutes after the catalyst addition and/or the use of a vacuum during the heating of polycaprolactone triols to a molten state. Preferred polycaprolactone hexols suitable as ingredients in the coating compositions of this invention have an average molecular weight of from 600 to 1500.

The polymer/polyols that can be used to prepare the coating compositions of this invention are known materials. Such polymer/polyols can be produced by polymerizing one or more ethylenically unsaturated monomers dissolved or dispersed in a base polyol in the presence of a free radical catalyst. The production of polymer/polyols is more fully described in U.S. Reissue 28,715, 29,118, 3,652,639 and 29,014, U.S.-A-3,950,317, 4,208,314, 4,104,236, 4,172,825 and 4,198,488.

While poly(oxypropylene) polyols are preferred, substantially any of the polyols previously used in the art to make polymer/polyols can be used as the base polyol. Illustrative of the base polyols useful in producing polymer/polyol compositions are the polyether polyols such as polyhydroxyalkanes and polyoxyalkylene polyols. Among the base polyols which can be employed are those selected from one or more of the following classes of compositions, alone or in admixture, known to those skilled in the art and described more fully hereinabove:

(a) Alkylene oxide adducts of polyhydroxyalkanes;
(b) Alkylene oxide adducts of non-reducing sugars and sugar derivatives;
(c) Alkylene oxide adducts of phosphorous and polyphosphorous acids;
(d) Alkylene oxide adducts thereof of polyphenols;
(e) The polyols from natural oils, such as castor oil. The most preferred base polyols employed in the polymer/polyols, which are useful as ingredients in the coating compositions of this invention, include the poly(oxypropylene) polyols. It should be appreciated that a blend or mixture of more than one base polyol can be utilized, if desired, to form the polymer/polyol.

Conceptually, the monomers used in preparing the polymer/polyols can comprise any ethylenically unsaturated monomer or monomers. A variety of monomers are disclosed in the patents relating to polymer/polyols previously referred to. The selection of the monomer or monomers used will depend on considerations such as the relative cost of the monomers and the product characteristics required for the intended application.

The preferred monomer and monomer mixture used to make the polymer portion of the polymer/polyols are acrylonitrile and a mixture of acrylonitrile and styrene, respectively. The relative weight proportions of acrylonitrile to styrene can range from 80:20 to 20:80. It may be desirable in some applications to utilize, with acrylonitrile, a comonomer other than styrene. Representative examples of suitable comonomers include methyl methacrylate, vinyl chloride and vinylidene chloride.

The polymer and polyol content of the polymer/polyols can vary within wide limits depending upon the requirements of the anticipated end use application. In general, the polymer content will vary from 10 to 50 percent, based upon the weight of the polymer/polyol. The polyol content of the polymer/polyols varies from 50 to 90 percent, based upon the weight of the polymer/polyol.

The polymer/polyols may, if desired, be blended with other conventional polyols described hereinabove to reduce the polymer content to the level desirable for the particular end use application. Blends in which the resulting polymer content is as low as 4 percent of the total weight of the blend or even less may be useful in the coating compositions of this invention.

The most preferred classes of polyols employed in the coating compositions of this invention are the polycaprolactone polyols such as those sold under the trademarks TONE-0200, TONE-0201 and TONE-0305 commercially available from Union Carbide Corp., the dihydroxyl functional polytetramethylene oxide polyols, such as sold under the trademarks Polymeg® 650, 1000 and 2000 commercially available from Quaker Oats Company, Merchandise Mart Plaza, Chicago, Illinois 60654; and Terathane® 650, 1000, 2000 and 2900, commercially available from DuPont Chemicals and Pigments Dept., Wilmington, Delaware 19898; the polymer/polyols, such as sold under the trademarks NIAX® Polymer Polyols 31-23 and 34-28 commercially available from Union Carbide Corporation, and, of course, the ethylene oxide and propylene oxide adducts including ethylene glycol, diethylene glycol, the poly(oxyethylene) glycols; propylene, dipropylene and tripropylene glycols; the poly(oxypropylene) glycols, triols and higher functionality polyols such as sold under the marks LHT-67, LHT-112, and LG-56, all commercially available from Union Carbide Corp.

A preferred alkylene oxide derived polyol suitable for use in the coating compositions of this invention has the following formula:

$$R_6 \left[O-(\underset{\displaystyle CH_3}{\underset{|}{CH_2}}-CH-O)_n-H \right]_3$$

wherein R_6 is an alkyl group of 3 to 10 carbon atoms, preferably 3 carbon atoms, and n is an integer of from 10 to 25. These polyols also include poly(oxypropylene-oxyethylene) polyols; however, desirably, the oxyethylene content should comprise less than 80 percent of the total and preferably less than 60 percent. The ethylene oxide, when used, can be incorporated in any fashion along the polymer chain. Stated another way, the ethylene oxide can be incorporated either in internal blocks, as terminal blocks, such as the propylene oxide polyols capped with ethylene oxide, i.e., such as sold under the trademarks NIAX® Polyols 11-27 and 11-34 and E-474, commercially available from Union Carbide Corp., or may be randomly distributed along the polymer chain. As is well known in the art, the polyols that are most preferred herein contain varying small amounts of unsaturation. Unsaturation, in itself, does not affect in any adverse way the formation of the coating compositions in accordance with the present invention.

Other representative examples of preferred organic polyols that may be employed in the coating compositions of this invention include copolymers of hydroxypropyl and hydroxyethyl acrylates and methacrylates with other free radical-polymerizable monomers, such as acrylate esters, vinyl halides, vinyl acetate or styrene; copolymers containing pendent hydroxy groups formed by hydrolysis or partial hydrolysis of vinyl acetate copolymers, polyvinylacetal resins containing pendent hydroxyl groups; modified cellulose polymers, such as hydroxyethylated and hydroxypropylated cellulose; hydroxy-terminated polyesters and hydroxy-terminated polyalkadienes. The polyester polyols are the reaction products of polyfunctional organic carboxylic acids and polyhydric alcohols and include, for example, poly(hexamethylene adipate), poly(ethylene adipate), and poly(butylene adipate).

Many of these organic polyols can be prepared by conventional methods and are commercially available from a number of manufacturers, such as, polyvinylacetal resins commercially available from Monsanto Chemical Company, 800 No. Lindbergh Blvd., St. Louis, Missouri 63166, and sold under the trademarks Butvar® B-72A, B-73, B-76, B-90 and B-98 and Formvar® 7/70, 12/85, 7/95S, 7/95E, 15/95S and 15/95E; an aliphatic polyester diol commercially available from Rohm and Haas Co., Independence Mall West, Philadelphia, Pennsylvania 19105, sold under the trademark Paraplex® U-148; saturated polyester polyols commercially available from Mobay Chemical Company, Penn-Lincoln Parkway East, Pittsburgh, Pennsylvania 15205, sold under the trademarks Multron® R-2, R-12A, R-16, R-18, R-38, R-68, and R-74; a hydroxypropylated cellulose having an equivalent weight of approximately 100 commercially available from Hercules, Inc., 910 Market Street, Wilmington, Delaware 19899, sold under the trademark Klucel® E; and a cellulose acetate butyrate ester having a hydroxyl equivalent weight of approximately 400 commercially available from Eastman Kodak Co., Organic Chemicals Dept., 343 State Street, Rochester, New York 14650, as Alcohol Soluble Butyrate, or other commercially available cellulose acetate butyrates.

The poly(active hydrogen) organic compounds utilized in the coating compositions of this invention can be mixtures or blends of organic polyols. For example, when utilizing a polycaprolactone polyol, it may be desirable to mix or blend one or more of a propylene oxide polyol, a propylene oxide polyol capped with ethylene oxide, a polytetramethylene oxide polyol or a polymer/polyol therewith. Other mixtures or blends may similarly be used if desired.

Other compounds which can be used in conjunction with the cycloaliphatic epoxides in the compositions of the present invention include cyclic vinyl ethers, described above, and linear vinyl ethers.

The linear vinyl ethers are well known in the art, and many are commercially availble. The vinyl ethers include the alkyl vinyl ethers, the aryl vinyl ethers, the divinyl ethers, the alpha and the beta substituted vinyl ethers and the functionally substituted vinyl ethers. The alkyl vinyl ether monomers include:

Methyl, ethyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, n-amyl, isoamyl, 1,2-dimethylpropyl, n-hexyl,1,2,2-trimethylpropyl, 2-ethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, diisopropylmethyl, n-octyl, 2-ethylhexyl, 1-methylheptyl; 2,2-dimethylhexyl, n-decyl, 2,2-dimethyloctyl, 2,2-dimethyldecyl,n-tetradecyl; 2,2-dimethyldodecyl, n-hexadecyl, 2-2-dimethyltetradecyl, n-octadecyl, and oleyl viny ethers.

The aryl vinyl ether monomers include: phenyl, o-cresyl, p-cresyl, p-chlorophenyl, 2,4-dichlorophenyl, 2,4,6-trichlorophenyl, alphanaphthyl, and beta-naphthyl vinyl ethers.

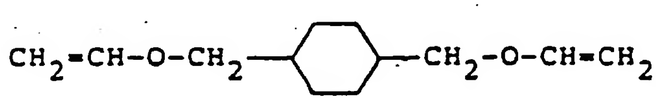
The divinyl ethers include the following:

$CH_2 = CH\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}CH = CH_2$
$CH_2 = CH\text{-}O\text{-}(CH_2)_3\text{-}O\text{-}CH = CH_2$

$$\underset{\displaystyle CH_3}{CH{=}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}\overset{}{\underset{|}{CH}}\text{-}O\text{-}CH{=}CH_2}$$

$CH_2 = CH\text{-}O\text{-}(CH_2)_6\text{-}O\text{-}CH = CH_2$
$CH_2 = CH = (O\text{-}CH_2\text{-}CH_2)_2\text{-}O\text{-}CH = CH_2$
$CH_2 = CH\text{-}(O\text{-}CH_2\text{-}CH_2)_3\text{-}O\text{-}CH = CH_2$
$CH_2 = CH\text{-}O\text{-}(CH_2)_4\text{-}O\text{-}CH = CH_2$

$CH_2 = CH\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_4\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}CH = CH_2$



(cis and trans) esterdiol divinyl ethers.

The alpha and beta substituted vinyl ethers including the following:
methyl alpha-methylvinyl ether,
methyl beta-chlorovinyl ether, methyl alpha-methylvinyl ether (cis) (trans),
methyl beta-chlorovinyl ether,
ethyl alpha-ethylvinyl ether,
ethyl alpha-methylvinyl ether (cis) trans),
ethyl alpha-phenylvinyl ether,
isopropyl beta-methylvinyl ether (cis) (trans),
n-butyl-alpha-methylvinyl ether (cis) (trans)
isobutyl-alpha-methylvinyl ether (cis) (trans), and
t-butyl-alpha-methylvinyl ether (cis) (trans).

Functionally substituted vinyl ethers are of the formula $CH_2=CHOR$, wherein R is selected from: CH_2CH_2OH, $CH_2CH_2CH_2CH_2OH$, CH_2CH_2Cl, $CH_2CH_2OCH_3$, CF_3, $CF(CF_3)_2$, $CF(CF_3)(CF_3Cl)$, $CF(CF_2Cl)_2$, $CH_2CH_2OCH_2CH_2OH$, $CH_2CH_2CHOHCH_3$, $CH_2CH_2OCH_2CH_2OCH_3$, $CH_2CH_2OCH_2CH_2OC_2H_5$, and $CH_2CH=CH_2$.

Other additional ingredients which can be used in conjunction with the cycloaliphatic epoxides include poly(vinyl halides) such as poly(vinyl chlorides), poly(vinyl esters) such as poly(vinyl acetate), polycaprolactones with structures as discussed above in conjunction with polycaprolactone polyols and copolymers of vinyl halides with vinyl esters, glycidyl acrylates, hydroxyalkyl acrylates, and mixtures of such monomers.

To photocopolymerize the compositions of the present invention in the presence of radiation, a photoiniator is used which will produce a cationic catalyst, including Bronsted-Lowry or Lewis acids, upon exposure to radiation in solution. The photoinitiator can be used in any suitable amount, but an advantage of the present invention is that much higher reaction or cure rates can be attained with even less than the normal proportions of photoinitiator; conversely, if an increased cure rate is not needed, a greatly reduced quantity of the costly photoinitiator can be sufficient. This not only reduces the cost of the composition, but can also be advantageous where it is desirable to minimize the amounts of metal ions or other photoinitiator residues in the cured coating, for example, in the production of nonconductive components of semiconductor devices. Using even relatively small amounts of the photoinitiator, high cure rates can be produced to allow almost any curing line speed desired.

Conventionally, such photoinitiators are used in photocurable compositions containing epoxides in proportions ranging from 0.1 to 30 parts by weight per 100 parts by weight of the epoxides. With the present invention, cure rates at least as fast as those obtained with such conventional quantities of photoinitiator can be obtained by using proportions of photionitiator ranging from 0.05 to 20 weight percent of the total composition. The higher proportions in this range may be used in the curing of pigmented compositions or producing very high curing speeds. Relatively low proportions can be used, preferably in the range of from 0.1 to 15 weight percent, and most preferably from 0.5 to 5 weight percent. In an embodiment in which the quantity of photoinitiator is to be minimized, the photoinitiator can be from 0.05 to 1 weight percent of the total composition. Alternatively, the photoinitiator can be present as from 0.01 to 10 weight percent of the cycloaliphatic epoxide in the composition.

In the method of the present invention, an effective amount of a cyclic ether-containing compound is included in the epoxide composition to be cured, allowing a reduced amount of photoinitiator to be used (a fraction of the amount normally used with a curable composition lacking such cyclic ether, usually less than half such amount) and at least a twofold increase in cure rate as reflected by line speed to be obtained. Alternatively, the amount of photoinitiator can be greatly reduced, for example, to a level less than one-fifth that normally required for curing a curable composition lacking such cyclic ether, and the reaction rate retained as approximately the same. Using amounts of photoinitiators conventionally used in the photocuring of comparable compositions lacking the cyclic ether, substantial increases in the cure rate can be obtained, amounting to tenfold, twentyfold or even greater.

Curing speeds in the industry are generally represented by the line speeds which can be maintained to produce the desired degree of curing in a given type of coating, using particular curing apparatus. The actual times of exposure to the curing lamp or other radiation source will depend upon the length and strength of the source as well as the line speed. The compositions of the present invention can be cured effectively in exposure times ranging from 0.01 to 50 seconds, preferably from 0.1 to 20 seconds, and most preferably from 1 to 10 seconds. Those skilled in the art will recognize that effective curing represents a state of cure such that polymerization has been initiated and that further cure can take place as a function of time and/or under the influence of thermal energy after the radiation source no longer impinges on the coating being cured. That is, systems cured with onium salts can continue to cure in the absence of radiation after the photoinitiator has been photolyzed or decomposed into its active species.

The photoinitiator can be added to the composition in the appropriate proportion just before curing, or included in appropriate proportions in prepared compositions which are to be shipped and/or stored. It has been discovered that such compositions containing photoinitiator are surprisingly stable provided they are protected from light.

The photoinitiators which can be used in the present invention include one or more of a metal fluoroborate and a complex of boron trifluoride, as described in U.S. -A-3,379,653; a bis-(perfluoroalkylsulfonyl) methane metal salt, as described in U.S. -A-3,586,616; an aryldiazonium compound, as described in U.S. -A-3,708,296; an aromatic onium salt of Group VIa elements, as described in U.S. -A-4,058,400; an aromatic onium salt of Group Va elements, as described in U.S. -A-4,069,055; a dicarbonyl chelate of a Group IIIa-Va element, as described in U.S. -A-4,086,091; a thiopyrylium salt, as described in U.S. -A-4,139,655; a Group VIa element having an MF_6 anion where M is selected from P, As and Sb, as described in U.S. -A-4,161,478; a triarylsulfonium complex salt, as described in U.S. -A-4,231,951; and an aromatic iodonium complex salt and an aromatic sulfonium complex salt, as described in U.S.-A-4,256,828. Preferred photoinitiators include polyarylsulfonium complex salts, aromatic sulfonium or iodonium salts of halogen-containing complex ions, and aromatic onium salts of Group IIIa, Va and VIa elements. Some of such salts are commercially available, such as those sold under the trademarks FC-508 or FX-512 (polyarylsulfonium hexafluorophosphate) and FC-509 (available from 3M Company), and UVE-1014 (polyarylsulfonium hexafluoroantimony salt available

Presently preferred photoinitiators include aromatic onium salts of phosphorus, sulfur, arsenic, iodine and antimony.

If desired, the efficiencies of the various photoinitiators useful in the present invention can be increased by the use of photosensitizers known to those skilled in the art. Such compounds absorb radiation (usually visible light) in a region of the spectrum in which the photoinitiator is transparent and then transfer the absorbed energy by one mechanism or another to the photoinitiator, inducing its photolysis. In addition to improving the overall efficiency of photoinitiators by increasing their effective light absorption, such photosensitizers make it possible to carry out photopolymerization using different portions of the radiation spectrum, e.g., visible light instead of or in addition to UV light.

Suitable photosensitizers for diaryliodonium salts are disclosed by Crivello and Lam in the Journal of Polymer Science, Chemical Education, Vol. 16, pp. 2441-51 (1978), while suitable photosensitizers for triarylsulfonium salts are disclosed in U.S. -A-4,069,054 and by Crivello and Lam (perylene) in The Journal of Polymer Science, Chemical Education, Vol. 17, pp. 1059-65 (1979).

As known to those skilled in the art, photosensitizers comprising amines or other basic groups should be used only in minor amounts which will not interfere with the photocopolymerization reaction.

The compositions of the present invention may include additives, such as oils, particularly silicone oil, surfactants, such as silicone-alkylene oxide copolymers and acrylic polymers, sold under the trade names such as the Modaflows (obtained from Monsanto Chemical Co.), silicone oil containing aliphatic epoxide groups, fluorocarbon surfactants; low molecular weight alcohols; products sold under the Cellosolve® trademark, such as butyl Cellosolve®; carbitols, such as butyl carbitol and diethyleneglycol.

If desired, one may include in the compositions of this invention various conventional non-basic fillers (e.g., silica, talc, glass beads or bubbles, clays, powdered metal such as aluminum, silver, zinc oxide, etc.) and other additives such as viscosity modifiers, rubbers, tackifying agents, pigments, solvents or diluents and the like.

The photocopolymerizable compositions of this invention are particularly suitable in a variety of applications in the fields of protective coatings and graphic arts due to their flexibility, impact resistance, abrasion resistance, hardness and adhesion to rigid, resilient and flexible substrates, such as metal, plastic, rubber, glass, paper, wood and ceramics. They can be cured for use as metal and plastic finishes, coatings for cans, electronic components, and appliances, and as inks, adhesives and sealants. These compositions can be cured much more rapidly than prior art compositions, and reduced quantities of the costly photoinitiator can be used, thus markedly reducing the cost of a formulated coating.

The photopolymerization or radiation curing of the compositions of the invention occurs upon exposure of the compositions to any source of radiation emitting actinic radiation to a wavelength within the ultraviolet and visible spectral regions. Suitable sources of radiation include mercury, xenon, carbon arc lamps, and sunlight. Exposure times may be broadly from less than 1 second to 10 minutes or more depending upon the amounts of particular polymerizable materials and photoinitiator being utilized and depending upon the radiation source type and dimensions, the substrate distance from the source and the thickness of the

coating to be cured. An advantage of the present invention is that good cures can be obtained in relatively brief exposure times, as described above. The compositions may also be photopolymerized by exposure to gamma rays, X-rays or electron beam irradiation. Generally speaking, the necessary dosage is from less than 1 megarad to 100 megarads or more.

The compositions of this invention may be prepared simply by mixing the formulation ingredients together, preferably under "safe light" conditions when the photoinitiator is incorporated.

In accordance with the present invention, the proportions of the ingredients of the composition and the photoinitiator are such that relatively brief radiation exposures can be used, so as to permit high line speeds for the curing and other processes.

EXAMPLES

The following Examples serve to give specific illustrations of the practice of this invention.

The numbered examples represent the present invention. The lettered examples do not represent the present invention and are for comparison purposes.

The following designations used in the examples and elsewhere in the present application have the following meanings:

ABBREVIATION	DEFINITION
Butyl Cellosolve®:	An ethylene glycol monobutyl ether obtained from Union Carbide Corp.
Diglycidyl Ether 1:	Epon® 828, A diglycidyl ether of Bisphenol A that has an equivalent weight of 185-192, obtained from Shell Chemical Co., Box 2463, Houston, Texas 77001.
Diglycidyl Ether 2:	Epon® 1001, A diglycidyl ether of Bisphenol A that has an equivalent weight of 450-550, obtained from Shell Chemical Co.
Epoxy 1:	3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, theoretical molecular weight of 274, obtained from Union Carbide Corp.

Epoxy 2:	Bis-(3,4-epoxycyclohexyl methyl)adipate, obtained from Union Carbide Corp.
Epoxy 3:	2-(3,4-Epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-meta-dioxane with an average epoxy equivalent weight of 133 to 154, obtained from Union Carbide Corp.
Epoxy 4:	Bis(2,3-epoxycyclopentyl) ether, obtained from Union Carbide Corp.
MTHP:	2-methoxytetrahydropyran
M.W., m.w.:	Molecular weight, number average, unless otherwise indicated.
Photoinitiator 1:	UVE-1014, A solution of a polyarylsulfonium hexafluoroantimony salt with a specific gravity of 1.39 and a Brookfield viscosity of 74 mPa·s centipoise at 25°C (obtained from General Electric Co., Polymers Product Dept., Pittsfield, MA 01201.)
Photoinitiator 2:	FC-508, A solution of a polyarylsulfonium hexafluorophosphate with a specific gravity of 1.33 and a Brookfield viscosity of about 4,000 mPa·s at 25°C (obtained from 3M Co., Chemical Division, 2501 Hudson Road, St. Paul, MN 55119.)

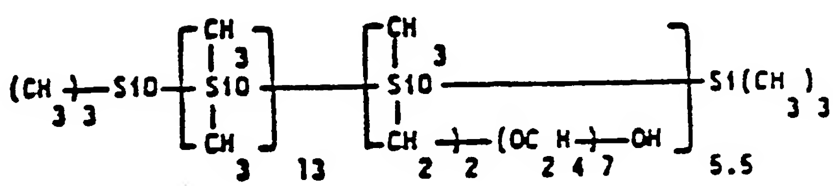
Polyol 1: A trihydroxyfunctional polycaprolactone polyol with an average hydroxyl number of 310 and an average molecular weight of 540. (Obtained from Union Carbide Corp., Old Ridgebury Road, Danbury, CT 06817).

Polyol 2: A propylene oxide polyol with an average hydroxyl number of 112.0 and a hydroxyl functionality greater than 2.0, obtained from Union Carbide Corp.

Polyol 3: A propylene oxide polyol with an average hydroxyl number of 67.0 and a hydroxyl functionality greater than 2.0, obtained from Union Carbide Corp.

Polyol 4: A propylene oxide polyol that has been partially end capped with 15% ethylene oxide to yield a high primary hydroxyl content polyol. It has a hydroxyl number of 28 and a functionality greater than 2.0, obtained from Union Carbide Corp.

Surfactant: A silicone surfactant with the structure



obtained from Union Carbide Corp.

THF: Tetrahydrofuran

THP: Tetrahydropyran

%: Percent by weight, unless otherwise designated

LABORATORY EXPERIMENTAL PROCEDURE

Preparation of 2-Methoxytetrahydropyran

A 2-liter hydrogenation reactor was cleaned and dried. 50 grams of Raney Nickel and 1200 grams of 2-methoxydihydropyran were charged to the reactor and the vapor space was purged with hydrogen. Then, while agitating the system, the temperature was raised to 40°C and the hydrogen pressure was raised to 69 bar (1000 psig). This temperature and pressure were maintained until no further hydrogen absorption occurred. The temperature was then slowly increased to 100°C. When the hydrogen uptake ceased at this temperature, the system was cooled to 30°C, carefully vented, and the product was removed. This crude product was refined by distillation using a 10-tray distillation column. The cut (958 grams from a charge of 1130 grams) that was obtained at a kettle temperature of 135°C and a still head temperature of 128°C was collected as 2-methoxytetrahydropyran.

Coating and Testing Procedures

In these examples, the coating of test panels consists of a 3-step procedure. First, a coating composition is prepared by mixing the components well in an amber-colored bottle (to protect against adverse effects of light). The resulting blended composition is then coated onto a Bonderite 37 steel panel using a Number 20 wire-wound rod. The coated panel is then cured using a mercury vapor ultraviolet light source at a predetermined linear rate. At least one pass through the zone of the light source is made.

After the panel has cooled to room temperature (i.e., from 40-50°C to 25°C), the coating is tested for tackiness, and for solvent resistance (a measure of the degree of cure) by rubbing the coating with a cheesecloth saturated with acetone. The coating is further tested for various physical properties, using at least one of the test procedures described below.

The procedures used to test coatings cured with the compositions of this invention were as follows:

Solvent Resistance (Double Acetone Rubs)

A measure of the resistance of the cured film to attack by acetone in which a film coating surface was rubbed with an acetone soaked cheesecloth back and forth with hand pressure. A rub back and forth with hand pressure over the film coating surface with the acetone soaked cheesecloth was designated as one "double acetone rub". The effect that a certain number of double acetone rubs had on the film coating surface was reported by a number in parentheses following the number of double acetone rubs. The rating system for evaluating acetone resistance for a given number of double acetone rubs was as follows:

Number in Parentheses After Number of Rubs

(1) No change in coating appearance.
(2) Scratched surface.
(3) Dulled, marred, some coating removed.
(4) Breaks in coating appearance.
(5) About one-half of the coating removed.

Pencil Hardness - ASTMD-3363-74

The rating system for pencil hardness was as follows:

Crosshatch Adhesion

Refers to a test using 10 parallel, single-edges, razor blades to scribe test films with 2 sets of perpendicular lines in a crosshatch pattern. Ratings are based on the amount of film removed after applying and subsequently pulling a contact adhesive tape (Scotch Brand 606) away from the surface of a scribed coating at a 90 degree angle in a fast, rapid movement. It is important to carefully apply and press the tape to the scribed coating to eliminate air bubbles and provide a good bond because adhesion is reported as the percent of film remaining on the substrate, with a 100 percent rating indicating complete adhesion of the film on the substrate.

Reverse or Face Impact Resistance

Measures the ability of a given film to resist rupture from a falling weight. A Gardner Impact Tester using an 3.6 kg (8 pound) dart is used to test the films cast and cured on the steel panel. The dart is raised to a given height in cm (inches) and dropped onto the reverse or face side of a coated metal panel. The cm (inches) times kg (pounds), designated cm.kg (inch-pounds), absorbed by the film without rupturing is recorded as the reverse or face impact resistance of the film.

COMPARATIVE EXAMPLE A

This example illustrates the photocuring of 2-methoxytetrahydropyran, using ultraviolet light and a photoinitiator which forms a cationic catalyst. 9.6 grams of 2-methoxytetrahydropyran (a clear liquid) and 0.4 gram of Photoinitiator 1 were placed in an amber-colored bottle and mixed well. The blend was then coated onto a Bonderite 37 steel panel with a Number 20 wire-wound rod. The coated panel was then cured with a 100 W per 2,54 cm (inch), medium-pressure, mercury-vapor diffuse light source (Source 1) at 10 m/min. (30 fpm). After one pass under this UV-light source, the coating was still liquid so it was passed twice or more under the light source. After the third pass, the coating was tacky; and, it was noticed that it became darker brown in color with each pass under the light source. After the panel cooled to room temperature (i.e., from 40-45°C to 25°C), it still had a tack. The coating was tested for solvent resistance, which is a measure of the degree of cure, by rubbing the coating with a cheesecloth saturated with acetone. The results of this example are presented in Table 1.

TABLE 1

Time After UV Exposure	Comment	Double Acetone Rubs
2 Hours	Light tack	2(5)
5 Hours	Light tack	2(5)
3 Days	Tack free	2(5)

This example demonstrates that 2-methoxytetrahydropyran alone does respond to a cationic cure mechanism, but the response is sluggish and the product produced is apparently of low molecular weight due to the rapid solubility in acetone. In addition, the dark color formation is not a highly desirable feature for many applications, since clear coatings could not be made and colors would be limited to brown or black.

EXAMPLE 1

This example illustrates the copolymerization of the 2-methoxytetrahydropyran of Example A in admixture with an epoxy compound. The experimental procedure above in Example A was used in this example with the following exceptions:

To 5 grams of the mixture prepared in Example A, 5 grams of Epoxy 1 and 3 drops of silicone surfactant were added. These ingredients were mixed and coated onto panels and cured with the UV source as described in Example A at various linear rates. The UV-exposed coatings had the solvent resistance properties presented in Table 2.

TABLE 2

m/min	Cure Rate (fpm)	Double Acetone Rubs: ~2 Hours After UV Exposure	Double Acetone Rubs: ~5 Hours After UV Exposure
9.2	(30)	100(1)	Not Measured
18.2	(60)	100(3)	100(1)
27.4	(90)	54(4)	100(1)
36.5	(120)	35(4)	100(1)
54.7	(180)	25(4)	100(1)
63.8	(210)	33(4)	100(1)
79.0	(260)	30(4)	100(2)
92.0	(300)	35(4)	100(1)

At cure rates up to 79 m/min (260 fpm), the coatings were tack free when warm immediately after exposure to the UV source. At 92 m/min (300 fpm), there was a very slight tack to the coating immediately after UV exposure; but, it was tack free 10-15 seconds after UV exposure. Although coatings cured at the higher speeds were not as resistant to solvents when tested 2 hours after UV exposure, at 5 hours after exposure, the samples were found to be uniformly resistant. No attempt was made to further increase the cure rate. This system contained approximately 2 percent of Photoinitiator 1.

This example illustrates the startling fact that when combined with Epoxy 1, 2-methoxytetrahydropyran undergoes extremely rapid copolymerization and that the two compounds are synergistic to each other in the curing of these systems.

Other properties of the coatings cured at the various rates are presented in Table 3. The properties were measured 3 days after UV exposure.

TABLE 3

Physical Properties of Coatings Cured at Various Rates, 3 Days After UV Exposure

Cure Rate m/min	Cure Rate (fpm)	Acetone Double Rubs	Pencil Hardness	Percent Crosshatch Adhesion	Gardner Impact, (in. lbs.) m·kg Face	Reverse
9.2	(30)	100(1)	F	98	(25)28.8	(<5) <5.76
18.2	(60)	100(1)	F	50	(25)28.8	(<5) <5.76
27.4	(90)	100(1)	H	97	(25)28.8	(<5) <5.76
36.5	(120)	100(1)	H	97	(25)28.8	(<5) <5.76
54.7	(180)	100(1)	H	99	(25)28.8	(<5) <5.76
63.8	(210)	100(1)	H	99	(25)28.8	(<5) <5.76
79.0	(260)	100(1)	H	100	(25)28.8	(<5) <5.76
92.0	(300)	100(1)	H	99	(25)28.8	(<5) <5.76

These data show that the physical properties of the coatings cured at linear velocities from 9.2 to 92 m (30 to 300 feet) per minute are substantially uniform, when tested 3 days after UV exposure.

EXAMPLES 2-9

These examples demonstrate that various amounts of 2-methoxytetrahydropyran (MTHP) can be blended with Epoxy 1 to produce systems that have unexpectedly high cure rates and that catalyst levels of 0.5 percent or less can be used to cure the systems.

The experimental procedure above in Example A was used in this example with the following exceptions:

The following ingredients (Table 4) were placed in amber-colored bottles, mixed well, and cured with the UV-curing device of Example A (UV Source 1) or a 300 watt 2.54 cm focused beam light source that used an A-bulb supplied by Fusion Systems (UV Source 2). The coatings were radiation cured at speeds of 9.2-92 m/min (30 to 300 fpm) and were found to be tack free either immediately after exposure to the radiation source or within 20 seconds after such exposure.

TABLE 4

Example	2	3	4	5	6	7	8	9
Ingredients, grams								
Methoxytetrahydropyran	3.92	2.9	2.0	1.0	3.96	3.98	2.9	3.92
Epoxy 1	5.88	6.9	7.8	8.8	5.94	5.97	6.8	5.88
Photoinitiator 1	0.20	0.20	0.20	0.20	0.10	0.05	--	--
Photoinitiator 2	--	--	--	--	--	--	0.40	0.20
Surfactant	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
% MTHP	39.2	29	20	10	39.6	39.8	28	39.2
% Photoinitiator	2.0	2.0	2.0	2.0	1.0	0.5	4.0	2.0

The physical properties of these cured coatings are given in the following Tables 5-7. It is apparent that the degree of crosslinking, as measured by solvent resistance or acetone double rubs, improved with aging in those coatings that have poor initial solvent resistance. This is due to the "dark cure" or cure that continues after exposure to the radiation source.

TABLE 5

Acetone Double Rubs as a Function of Time After Exposure to UV Source 1 at ~~100 FPM~~ 54.9 m/min [2]

	2 Hours	6 Hours	1 Day	5 Days
Example 2[1]	100(1)	100(1)	100(1)	100(1)
Example 3	100(1)	100(1)	100(1)	100(1)
Example 4	100(1)	100(1)	100(1)	100(1)
Example 5	100(1)	100(1)	100(1)	100(1)
Example 6	100(1)	100(1)	100(1)	100(1)
Example 7	100(1)	100(1)	100(1)	100(1)
Example 8	14(4)	20(4)	25(4)	70(4)
Example 9	18(4)	20(4)	24(4)	30(4)

1 When the system of Example 2 was cured at 92 m/min (300 fpm) (0.6 s... exposure), identical results were obtained.
2 Exposure time 1.0 second.

TABLE 6

Acetone Double Rubs as a Function of Time[2] After Exposure to UV Source 2 at ~~150 FPM~~ 45.7 m/min

	0.75 Hours	6 Hours	1 Day	5 Days
Example 2[1]	95(3)	100(1)	100(1)	100(1)
Example 3	100(1)	100(1)	100(1)	100(1)
Example 4	100(1)	100(1)	100(1)	100(1)
Example 5	100(1)	100(1)	100(1)	100(1)
Example 6	65(4)	100(1)	100(1)	100(1)
Example 7	35(5)	100(1)	100(1)	100(1)
Example 8	20(4)	40(4)	100(1)	100(1)
Example 9	10(5)	15(4)	25(4)	70(4)

1 Cure speed was 48.8 m/min (160 fpm) for Example 2.
2 Exposure time 0.25 second.

TABLE 7

Physical Properties of Coatings Cured at ~~30 FPM~~ 9.2 m/min[2] With UV Source 1, 5 Days After UV Exposure

Example	2	3	4	5	6	7	8	9
Acetone Double Rubs[1]	100(1)	100(1)	100(1)	100(1)	100(1)	100(1)	30(5)	15(5)
Pencil Hardness	H	2H	H	H	H	H	H	H
% Cross-hatch Adhesion	0	10	50	98	0	90	100	100
Gardner Impact								
Face, (in.lbs.)	(<5)	(15)	(15)	(25)	(<5)	(15)	(100)	(75)
cm·kg	<5.76	17.28	17.28	28.8	5.76	17.28	115.2	86.4
Reverse, (in.lbs.)	(<5)	(<5)	(<5)	(<5)	(<5)	(<5)	(<5)	(<5)
cm·kg	<5.76	<5.76	<5.76	<5.76	<5.76	<5.76	<5.76	<5.77

1 Except for Examples 8 and 9, acetone double rubs were determined one day after UV exposure.
2 Exposure time 6 seconds.

Examples A and 2 through 9 indicate that MTHP alone responds to UV curing with a photoinitiator present, but the reaction is sluggish. Surprisingly, combinations of MTHP with Epoxy 1 containing from 10 to 50 weight percent MTHP cure very rapidly. These combination systems respond when 0.5 weight percent (or even less) up to 4 weight percent (or even more) of a photoinitiator is present.

Thus in the examples developed to this point, it has been shown that MTHP alone will respond to UV cure in the presence of a photoinitiator, but the reaction is sluggish; combinations of Epoxy 1 and MTHP that contain from 10 to 50 weight percent MTHP cure very rapidly; the combination systems respond when 0.5 weight percent to 4 weight percent or more photoinitiator is present.

EXAMPLE 10

This example illustrates the performance of a different cycloaliphatic epoxide combined with MTHP and cured with UV light.

The experimental procedure above in Example A was used in this example with the following exceptions:

The following ingredients (Table 8) were placed in amber-colored bottles, mixed well, and coated/cured as described in Example 2 at rates of 9.2 m/min (30 fpm) 6 s exposure) and 54.9 m/min. (180 fpm) (1 s exposure). The coating cured at 9.2 m/min. (30 fpm) was tack free immediately after exposure to the UV light source and the coating cured at 54.9 m/min. (180 fpm) had a very slight tack immediately after UV exposure but was tack free when it cooled to room temperature.

TABLE 8

MTHP	4.9 g.
Epoxy 2	4.9 g.
Photoinitiator 1	0.2 g.
Surfactant	0.05 g.

The coating cured at 9.2 m/min. (30 fpm) had an acetone double rub rating of 13(5) one day after UV exposure. Five days after UV exposure, and a pencil hardness of H, 100 percent crosshatch adhesion and >369 cm•kg (>320 in.lbs.) face and reverse Gardner impact resistance were noted.

EXAMPLES 11-13, COMPARATIVE EXAMPLES B AND C

These examples indicate that MTHP can be cocured with epoxides and polyols in the presence of a photoinitiator (Examples 11-13). Comparative Examples B and C indicate that mixtures of MTHP and polyols alone do not cure in the presence of a photoinitiator to yield useful coatings, inks, etc.

The following ingredients (Table 9) were placed in amber-colored bottles, mixed well, coated and cured as described in Examples 2-9.

TABLE 9

Example	11	12	13	B	C
MTHP, g	1.40	1.10	1.10	7.10	7.60
Epoxy 1, g	6.30	6.10	6.10	--	--
Polyol 2, g	0.90	--	--	--	--
Polyol 3, g	0.90	--	--	--	--
Polyol 1, g	1.10	2.60	2.60	2.50	--
Polyol 4, g	--	--	--	--	2.00
Butyl Cellosolve®, g	0.20	--	--	--	--
Photoinitiator 2, g	--	--	0.40	0.40	0.40
Photoinitiator 1, g	0.20	0.20	--	--	--
Surfactant, g	0.05	0.05	0.05	0.05	0.50

The coatings of Examples 11-13 were tack free when warm immediately after UV exposure and when cured at a rate of 9.2 m/min. (30 fpm). The coatings of Examples B and C were still liquid in nature - though there had been some increase in viscosity - after three passes under the UV source at 9.2 m/min (30 fpm) indicating that little if any reaction took place between the cyclic ether and the polyols. The same results were obtained for Examples 11-13 at cure rates of 45.7 m/min. (150 fpm); but at 54.9 m/min. (180 fpm), a very slight tack was noticed. This disappeared and the coatings were tack free when cooled to room temperature. No characteristic properties were determined for Examples B and C.

The properties of the coatings of Examples 11-13 are presented in Tables 10 and 11.

TABLE 10

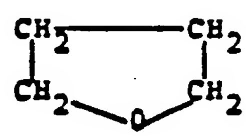
	Acetone Double Rubs When Cured at 54.9 m/min (180 fpm)			
	2 Hours	6 Hours	1 Day	5 Days
Example 11	100(1)	100(1)	100(1)	100(1)
Example 12	100(1)	100(1)	100(1)	100(1)
Example 13	65(4)	60(4)	100(1)	100(1)

TABLE 11

	Properties After 5 Days After 9.2 m/min (30 fpm) Cure (Acetone Rubs 1 Day After)		
	Example 11	Example 12	Example 13
Double Acetone Rubs	100(1)	100(1)	100(1)
Pencil Hardness	H	H	H
% Crosshatch Adhesion	50	100	100
Gardner Impact, (in. lbs.) cm·kg			
Face	(25) 28.8	(175) 201.6	(225) 259.2
Reverse	(<5) <5.76	(125) 144	(175) 201.6

EXAMPLES 14-17

These examples described the UV-light curing of tetrahydrofuran



(THF)-containing systems. They exemplify that other cyclic ethers can be used in this invention, including those which are unsubstituted, but that THF does not perform as well as 2-methoxytetrahydropyran.

Compositions containing the following ingredients (Table 12) were mixed, coated, and cured as described in the previous examples.

TABLE 12

Example	14	15	16	17
Tetrahydrofuran, g	9.6	4.8	1.9	3.5
Epoxy 1	--	4.8	7.7	3.6
Polyol 1, g	--	--	--	2.5
Photoinitiator 1, g	0.4	0.4	0.4	0.4

The coating of Example 14 that contained only THF evaporated from the panel before it could be carried to the UV-curing device. Attempts to put larger amounts on the panel were also unsuccessful, since the THF evaporated for the most part while in the curing device. There was some tacky material on the panel, which indicated that the THF would have given a sluggish cure if it had not evaporated first. The

coatings of Examples 15, 16 and 17 were tack free when warm immediately after UV exposure and when cured at 9.2 m/min. (30 fpm). At 18.4 m/min. (60 fpm), the surface of the coatings was tack free when warm, but it could be distorted. When cooled to room temperature (i.e., from ~40-45°C to 25°C), the films were hard and could not be distorted.

The properties of the coatings of Examples 15-17 are presented in Table 13.

TABLE 13

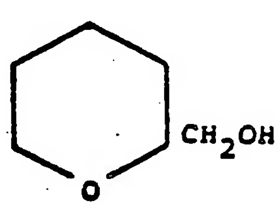
Physical Properties 1 Day After UV Exposure

	Example 15	Example 16	Example 17
Acetone Double Rubs			
(30 fpm) 9.2 m/min	100(1)[1]	100(1)[1]	35(4)
(60 fpm) 18.4 m/min	100(1)[1]	100(1)[1]	35(4)
Pencil Hardness			
(30 fpm) 9.2 m/min	5H	5H	F
(60 fpm) 18.4 m/min	5H	5H	F
% Crosshatch Adhesion			
(30 fpm) 9.2 m/min	100	100	100
(60 fpm) 18.4 m/min	100	100	100
Gardner Impact, (in. lbs.) cm.kg			
Face, (30 fpm) 9.2 m/min	(50) 57.6	(25) 28.8	(>320) >369
Reverse, (30 fpm) 9.2 m/min	(<5) <5.76	(<5) <5.76	(>320) >369
Face, (60 fpm) 18.4 m/min	(25) 28.8	(25) 28.8	(>320) >369
Reverse, (60 fpm) 18.4 m/min	(<5) <5.76	(<5) <5.76	(>320) >369

1 Measured after 1 hour.

EXAMPLES 18-22

This example illustrates attempts to polymerize tetrahydropyran-2-methanol



with UV-activated onium salts as a photoinitiator. This compound was obtained from the Aldrich Chemical

Company.

The following ingredients (Table 14) were blended and cured as described in Examples 2-9 using UV source 2, operating at a linear rate of 10 fpm (3.6 s exposure).

TABLE 14

Example	18	19	20	21	22
Ingredients, grams					
Tetrahydropyran-2-methanol	9.45	9.45	4.70	2.35	7.59
Epoxy 1	--	--	4.75	7.10	--
Epoxy 3	--	--	--	--	1.86
Photoinitiator 1	0.50	--	--	--	--
Photoinitiator 2	--	0.50	0.50	0.50	0.50
Surfactant	0.05	0.05	--	--	--

. The coating films of Examples 18 and 19 (without epoxy) were very fluid after three passes under the radiation source, which suggests that little or no polymerization took place. The coating films from Examples 20 and 22 were solid in nature but had a tack, suggesting that cure took place and that the films would have use as an adhesive, such as a pressure sensitive adhesive. The coating film of Example 22 was tack free when warm immediately after UV exposure. The properties of the cured coatings of Examples 20-22 are given below in Table 15.

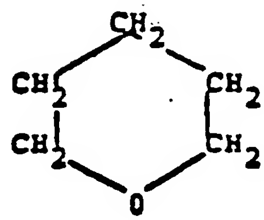
TABLE 15

Physical Properties 1 Day After UV Exposure

Example	20	21	22
Acetone Double Rubs	2(5)	4(5)	2(5)
Pencil Hardenss	3B	H	<5B
% Crosshatch Adhesion	100	97	100

EXAMPLES 23-33

These examples illustrate the UV-light curing of reactant blends containing tetrahydropyran, obtained from the Aldrich Chemical Co.



This compound functions well in curing such mixtures, but it does not perform as well as 2-methoxytetrahydropyran. The compound is volatile and has a tendency to evaporate before it cures when used alone or at high levels in coating systems. The systems are slow reacting, since 2 or 3 passes at 3-6 m/min (10-20 fpm) were required to effect cure of the systems described below.

The ingredients listed below (Table 16) were well mixed, applied to steel panels and cured as described in Example A, with the following exceptions: Examples 23 to 25 were run with UV source 2 at 3 m/min. (10 fpm) (3.6 s exposure), while Examples 26 to 33 were run with UV Source 2 at 6.1 m/min (20 fpm) (1.8 s exposure).

TABLE 16

Example	23	24	25	26	27	28	29	30	31	32	33
Ingredients, g											
Tetra-hydropyran	9.6	4.8	1.9	3.5	2.0	4.0	2.0	4.0	2.8	4.8	2.0
Epoxy 1	--	4.8	7.7	3.6	--	--	3.8	3.8	0.8	--	2.0
Polyol 1	--	--	--	2.5	--	--	--	--	--	4.8	2.0
Diglycidyl Ether 1	--	--	--	--	7.6	5.6	3.8	1.8	--	--	2.0
Diglycidyl Ether 2	--	--	--	--	--	--	--	--	2.0	--	--
Vinylcyclo-hexene Monoepoxide	--	--	--	--	--	--	--	--	2.0	--	1.6
Photo-initiator 1	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Surfactant	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05

These cured systems had the following properties one day after exposure to UV Source 2 at 3 or 6.1 m/min (10 or 20 fpm). No properties are listed for the system of Example 23 because it evaporated before cure was effected.

TABLE 17

Example	24	25	26	27	28	29	30	31	32	33
Physical Properties 1 Day After UV Exposure										
Double Acetone Rubs	100	100	20	100	70	100	100	20	2	25
Pencil Hardness	4H	4H	3H	3H	4H	4H	4H	3H	F	--
% Crosshatch Adhesion	100	100	100	100	100	100	100	100	100	100
Gardner Impact cm·kg	28.8	28.8	>369	115	86.4	28.8	28.8	17.3	>360	—
Direct, (in.lbs.)	(25)	(25)	(>320)	(100)	(75)	(25)	(25)	(15)	(>320)	--
Reverse (in.lbs.)	(<5)	(<5)	(>320)	(75)	(50)	(<5)	(<5)	(<5)	(>320)	
cm·kg	<5.8	<5.8	>369	86.4	57.6	<5.8	<5.8	<5.8	>369	
Properties after 10 min. 150°C Thermal Post Cure										
Double Acetone Rubs	100	100	100	100	100	100	100	100	--	80
Pencil Hardness	>6H	5H	2H	5H	5H	5H	5H	5H	--	4H-
% Crosshatch Adhesion	100	100	100	100	100	100	100	100	100	100
Gardner Impact cm·kg	28.8	28.8	>369	57.6	28.8	28.8	28.8	>369	—	>369
Direct, (in.lbs.)	(25)	(25)	(>320)	(50)	(25)	(25)	(25)	(>320)	--	(>320)
Reverse (in.lbs.)	(<5)	(<5)	(>320)	(15)	(<5)	(<5)	(<5)	(>320)	--	(>320)
cm·kf	<5.8	<5.8	>369	17.3	<5.8	<5.8	<5.8	>369	—	>369

The coating of Example 32 was relatively poor in nature and the polyol appeared to have exuded to the surface.

EXAMPLE 34

This example describes the UV light curing of blends that contain tetrahydropyran-2-methanol, obtained from the Aldrich Chemical Co.

The experimental procedure above in Example A was used in this example with the following exceptions:

When this compound was evaluated in combination with a variety of other epoxides and polyols, after three passes under UV Source 2, tacky coatings resulted. When the coatings were thermally postcured for 10 minutes, only one out of 14 coatings was tack free. Thus, it appears that this compound cures very poorly under the conditions employed.

EXAMPLES 35-37

These examples illustrate the formation of good cured coatings from mixtures of 2-methoxytetrahydropyran with another type of epoxide.

The following ingredients (Table 18) were placed in containers, mixed, cast onto steel panels and cured as described in comparative Example A.

The properties of the cured coatings (Table 18) indicate that high quality coatings were prepared. The coatings of Example 37 provided a very good combination of hardness and impact resistance.

TABLE 18

Example	35	36	37
Ingredients, g			
Epoxy 4	7.0	6.0	5.0
MTHP	3.0	3.0	3.0
Polyol 1	--	1.0	2.0
Photoinitiator 1	0.2	0.2	0.2
Surfactant	0.05	0.05	0.05
Properties			
Double Acetone Rubs	>100	>100	>100
Pencil Hardness	2H	3H	2H
% Crosshatch Adhesion	100	100	100
Gardner Impact, (in.lbs.) cm.kg			
Direct	(25) 28.8	(25) 28.8	(>320) >369
Reverse	(<5) <5.8	(<5) <5.8	(>320) >369

EXAMPLES 38-50

To determine the effect of room temperature aging on the shelf life of the very rapid curing coating systems of Examples 1 to 13, the solutions (coating formulations) were allowed to age from March 8, 1983, when they were prepared for Examples 1-11, B and C, until March 19, 1984. On this latter date, these coating solutions (except for Example 12, of which none remained) were again cast onto Bonderite 37 steel panels and cured at various rates with the UV Source 1. the results are presented in Table 19.

TABLE 19

Physical Properties of Coatings Aged One Year Before UV Curing

Example	38	39	40	41	42	43	44	45	46	47	48	49	50
Previous Ex. No.	1	2	3	4	5	6	7	8	9	10	11	B	C
Cure Speed, m/min (fpm)	45.75 (150)	91.5 (300)	45.75 (150)	45.75 (150)	45.75 (150)	45.75 (150)	45.75 (150)	30.5 (100)	45.75 (150)	45.75 (150)	45.75 (150)	9.7 (30)	9.7 (30)
Exposure s	1.2	0.6	1.2	1.2	1.2	1.2	1.2	1.8	1.2	1.2	1.2	6.0	6.0
Double Acetone Rubs	>100	>100	>100	>100	>100	>100	>100	60	12	>100	70	2	2
Pencil Hardness	2H	2H	2H	2H	H	2H	2H	H	H	2H	2H	--	--
% Cross-hatch Adhesion	100	100	100	100	97	100	100	100	100	100	100	--	--
Gardner Impact cm·kg (in.lbs) Direct	28.8 (25)	28.8 (25)	28.8 (25)	28.8 (25)	28.8 (25)	17.3 (15)	28.8 (25)	28.8 (25)	>369 (>320)	>369 (>320)	>369 (>320)	--	--
Reverse	<5.8 (<5)	<5.8 (<5)	<5.8 (<5)	<5.8 (<5)	<5.8 (<5)	<5.8 (<5)	<5.8 (<5)	<5.8 (<5)	>369 (>320)	173 (150)	346 (300)	--	--

From these results, it is readily apparent that the properties of coatings obtained from these systems are essentially the same as those from the systems cured over a year earlier. This is particularly significant in that very rapidly reacting systems, such as these 100% solids mixtures, can have short shelf lives. However, these systems remained active and yielded good properties over one year after their preparation when stored in the absence of ultraviolet light.

EXAMPLE 51

This example illustrates the radiation curing of mixtures of cycloaliphatic ethers and cycloaliphatic epoxides containing relatively small amounts of the cycloaliphatic ether. The experimental procedure above in Example A was used in this example with the following exceptions.

The ingredients of the mixture were 9.9 g Epoxy 1, 0.10 g MTHP, 0.4 g photoinitiator 1 and 0.05 g. Surfactant, with MTHP present as approximately 0.96 percent of the total composition or 1.0 percent based upon the MTHP and epoxide alone.

The coating was cured by passing it under UV Source 2 at a rate of 3 m/min (10 fpm) (approximately 3.8 seconds exposure). The cured panel was tack free when warm, immediately after ultraviolet light exposure. 24 hours after exposure, the coating passed 100 acetone double rubs, had no crosshatch adhesion, had a pencil hardness of 2H, and an impact resistance of 28.8 cm•kg (25 in-lb) when directly impacted and of less than 5.8 cm•kg (5 in-lbs when subjected to reverse impact. 9 days after UV exposure, the crosshatch adhesion had improved to 75 percent with no change in hardness. Thus, even very small proportions of the cycloaliphatic ether can produce mixtures which cure well, albeit at slower rates.

EXAMPLES 52-55

The experimental procedure above in Example A was used in this example with the following exceptions.

The ingredients shown in Table 20 were mixed, cast and cured by exposure to UV Source 2 at a rate of 3 m/min (10 feet per minute). (3.8 seconds exposure).

TABLE 20

Example	52	53	54	55
Ingredients, g				
MTHP	6.00	7.00	8.00	9.00
Epoxy 1	4.00	3.00	2.00	1.00
Photoinitiator 1	0.40	0.40	0.40	0.40
Surfactant	0.05	0.05	0.05	0.05
Percent MTHP	57.4	67.0	76.6	86.1

The exposed coatings of Examples 52 and 53 were tack free when warm immediately after UV exposure. The exposed coatings of Examples 54 and 55 were tacky when warm immediately after UV exposure. It was apparent that there had been some evaporation of coating from the system of Example 55 after UV exposure. When the coatings of Examples 54 and 55 were examined 24 hours after UV exposure, they were tack free.

The cured coatings of these examples had the following physical characteristics (Table 21) when they were determined 24 hours after UV exposure.

TABLE 21
Properties Of Coatings Cured With UV
Source 2 At 10 fpm, One Day After Exposure

Example	52	53	54	55
Double Acetone Rubs[1]	15	7	4	2
Pencil Hardness	F	B	3B	2H
% Crosshatch Adhesion	100	100	100	100
Gardner Impact				
Direct, (in-lbs) cm·kg	(75) 86.4	(75) 86.4	(75) 86.4	(75) 86.4
Reverse, (in-lbs) cm·kg	(15) 17.3	(<15) <17.3	(<15) <17.3	(<15) <17.3

1 These values represent the point at which about one-half of the coating was removed.

These data indicate that the mixtures cure more slowly as the proportions of MTHP are increased above about 75 percent of the total composition, and based upon the relatively low number of double acetone rubs attained, these coatings have less solvent resistance. While not wishing to be bound by theory, it is presently believed that this may be due to the formation of structures which are less crosslinked or more linear as the proportions of MTHP increase.

Certain properties were again examined nine days after the exposure to ultaviolet light. The double acetone rubs did not change. The hardness values were as shown in Table 22.

TABLE 22

Example 52..........2H
Example 53..........HB
Example 54..........H
Example 55..........4H

Thus, the hardness increased with the passage of time. Since the acetone resistance did not change, it is strongly suggested that the ingredients had further polymerized in a linear or non-crosslinked manner as time passed.

EXAMPLES 56-58

The experimental procedure above in Example A was used in these examples with the following exceptions.

The ingredients shown in Table 23 were mixed, cast, and cured by exposure to UV Source 2 at a rate of 3 m/min (10 feet per minute) (3.8 seconds exposure).

TABLE 23

Example	56	57	58
Ingredients, g			
MTHP	4.75	4.75	3.75
Epoxy 1	4.56	4.56	4.26
1,2-epoxydodecene	0.24	0.24	0.14
Triethylene glycol	--	--	0.14
Polyol 2	--	--	0.65
Polyol 3	--	--	0.61
Photoinitiator 1	--	0.40	--
Photoinitiator 2	0.40	--	0.40
Surfactant	0.05	0.05	0.05

The exposed coatings of Examples 56-58 were tack free when warm immediately after UV exposure. the cured coatings of these examples had the following physical characteristics (Table 24) when they were determined 24 hours after UV exposure.

TABLE 24

Properties Of Coatings Cured With UV Source 2 At 10 fpm, One Day After Exposure

Example	56	57	58
Double Acetone Rubs	65(4)	100(2)	100(3)
Pencil Hardness	4H	2H	2H
% Crosshatch Adhesion	75	98	100
Gardner Impact			
Direct, (in-lbs) cm.kg	(25) 28,8	(25) 28.8	(>320) >369
Reverse, (in-lbs) cm.kg	(<5) <5.8	(<5) <5.8	(>320) >369

The above examples illustrate that combinations of cycloaliphatic ethers and cycloaliphatic epoxides cure rapidly and effectively in the presence of a photoinitiator and ultraviolet light. The use of these components in coating systems, which can optionally contain other polymerizable components, permits much higher line speeds in coating processes and/or the use of reduced quantities of the costly photoinitiator. It is necessary to optimize a system for its end use by varying the amounts of the components in the system. The results of the above examples do not represent optimized coating systems, but are intended only to illustrate that the curing rate and amount of photoinitiator required can be varied by using various proportions of these components.

Claims

1. A composition suitable for curing by photopolymerization comprising at least one cyclic ether-containing compound and at least one cycloaliphatic epoxide containing at least one epoxy group, wherein the cyclic ether and the at least one epoxy group are contained in the same or different molecules.

2. The composition in accordance with claim 1 wherein the cyclic ether is a cycloaliphatic ether free of cyclic ethylenic unsaturation, preferably a vinyl ether or a cycloaliphatic ether having from 4 to 10 ring carbon atoms, preferably 2-methoxy tetrahydropyran, tetrahydropyran-2-methanol or tetrahydrofuran.

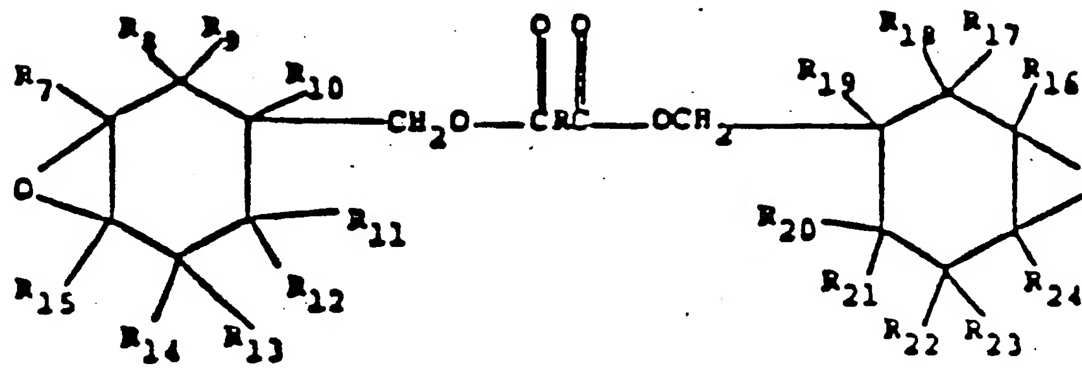
3. The composition in accordance with claim 2 wherein the cycloaliphatic ether ring contains at least one substituent selected from alkyl, aryl, alkoxy and hydroxyalkyl groups having from 1 to 10 carbon atoms, vinyl having from 2 to 4 carbon atoms, halide, nitro, sulfonyl and hydroxyalkyl groups reacted with oxyalkylene adducts, carboxylic acids or lactones.

4. The composition in accordance with claim 3 wherein at least one such substituent is located adjacent to the ether linkage of the cycloaliphatic ether.

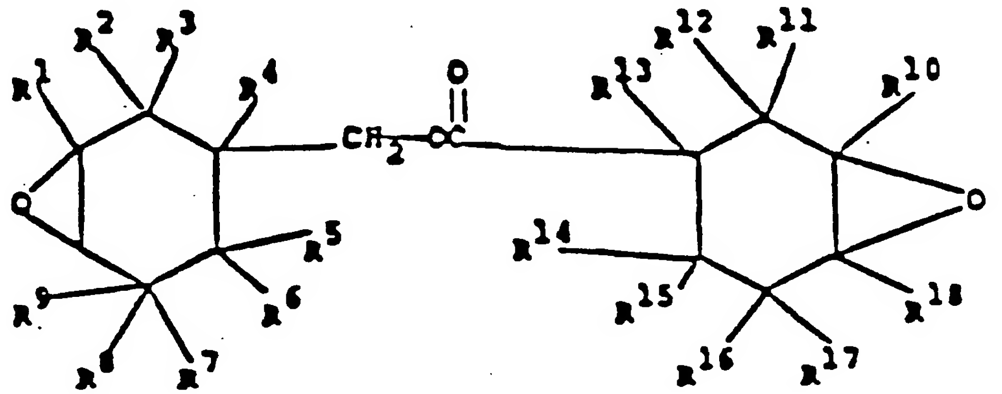
5. The composition in accordance with claim 1 wherein the cyclic ether-containing compounds comprises at least two rings containing ether linkages.

6. The composition in accordance with claims 1 to 5 wherein the cyclic ether-containing compound comprises from 5 to 60 weight percent of the total composition or from 5 to 70 weight percent of the mixture of the cycloaliphatic expoxide and the cyclic ether-containing compound.

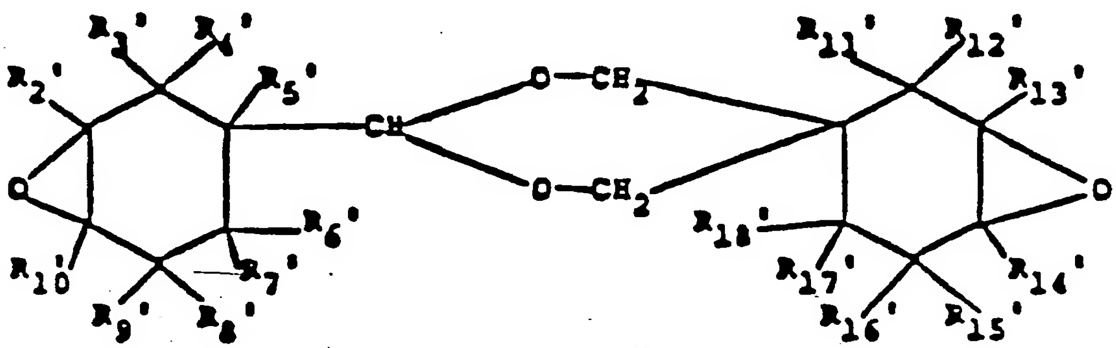
7. The composition in accordance with claims 1 to 6 wherein the cycloaliphatic epoxide is a diepoxide or an epoxide having the formula:



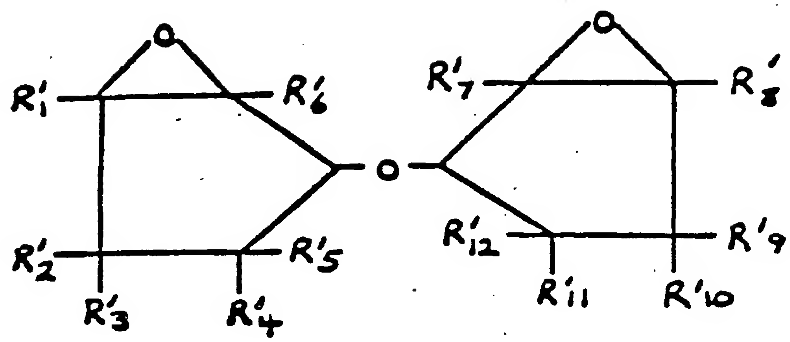
wherein R_7 to R_{24}, which can be the same or different, are hydrogen or alkyl radicals generally containing 1 to 9 carbon atoms; and R is a valence bond or a divalent hydrocarbon radical generally containing 1 to 10 carbon atoms; or having the formula:



wherein R^1 to R^{18}, which can be the same or different, are hydrogen or alkyl radicals generally containing 1 to 9 carbon atoms; or having the formula;



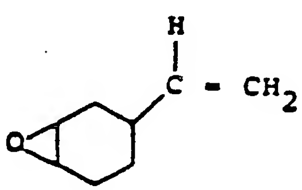
wherein the R's are the same or different and are monovalent substituents or monovalent hydrocarbon radicals; or having the formula:



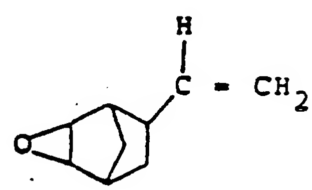
wherein the R's, which can be the same or different, are monovalent substituents such as hydrogen, halide or monovalent hydrocarbon radicals.

8. The composition in accordance with claim 7 wherein the cycloaliphatic epoxide is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis(3,4-epoxycyclohexylmethyl)-adipate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)-cyclohexane-metadioxane, bis(2,3-epoxycyclopentyl)-ether, vinylcyclohexene diepoxide, a mixture of bis(3,4-epoxycyclohexyl methyl)adipate and 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)-cyclohexane-metadioxane or 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylat and bis(3,4-epoxycyclohexylmethyl)-adipate.

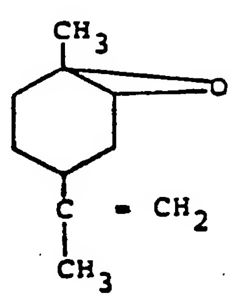
9. The composition in accordance with claims 1 to 7 wherein the cycloaliphatic epoxide is a glycidyl type epoxide or the epoxide comprises a substituted or unsubstituted cycloaliphatic monoepoxide and preferably the substituted cycloaliphatic monoepoxide contains substituents selected from alkyl groups of 1 to 9 carbon atoms, halogen atoms, oxygen, and ether, ester, hydroxyl and vinyl radicals; more preferably the substituted cycloaliphatic monoepoxide is a vinyl substituted cycloaliphatic monoepoxide or a vinyl cycloaliphatic monoepoxide of the following formulae:



, or



, or



the substituted cycloaliphatic monoepoxide is a hydroxyl substitued cylcoaliphatic epoxide.

10. The composition in accordance with claims 1 to 9 wherein the cycloaliphatic epoxide is blended with at least one epoxy compound selected from glycidyl type epoxides, aliphatic epoxides, epoxy cresol novolac resins, epoxy phenol novolac resins, polynuclear phenol-glycidyl ether-derived resins, aromatic and heterocyclic glycidyl-amine resins, hydantoin epoxy resins, epoxides of natural oils.

11. The composition in accordance with claim 1 wherein the cyclic ether and the at least one epoxy group are contained in separate rings of a single molecule having at least 2 rings or in a single ring structure having from 4 to 20 ring carbon atoms.

12. The composition in accordance with claims 1 to 11 further comprising at least one ingredient selected from poly(active hydrogen) organic compounds, vinyl ethers, glycidyl ethers, poly(vinyl halides), poly(vinyl esters) polylactones, and copolymers of vinyl halide and vinyl ester monomers.

13. The composition in accordance with claims 12 wherein the poly (active hydrogen) organic compound is selected from polyether polyols, polycaprolactone polyols, polyester polyols, acrylic polyols, vinyl polyols, and polymer/polyols, and mixtures thereof; the polyether polyol is selected from propylen oxide polyols, ethylene oxide polyols, propylene oxide polyols capped with ethylene oxide, and tetramethylene oxide polyols, and the vinyl ether is a cyclic vinyl ether or a linear vinyl ether.

14. The composition in accordance with claims 1 to 13 further comprising a photoinitiator which forms a cationic catalyst when irradiated in solution.

15. The composition in accordance with claim 14 wherein the photoinitiator is selected from diazonium salts, onium salts, and mixtures thereof; preferably the photoinitiator is an aromatic onium salt of an element of Groups IIIa, Va or VIa or comprises a polyarylsulfonium hexafluorophosphate, or a polyarylsulfonium hexafluoroantimony salt.

16. The composition in accordance with claim 15 wherein the photoinitiator is present in a reduced amount which is effective to produce a cure rate greater than that of a composition not comprising said cyclic ether containing compound, preferably photoinitiator comprises from 0.05 to 20 weight percent or from 0.5 to 5 weight percent, perferably from 0.05 to 1 weight percent of said composition.

17. The composition in accordance with claim 1 comprising from 5 to 70 weight percent of 2-methoxytetrahydropyran and at least one cycloaliphatic epoxide selected from 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis-(3,4-epoxycyclohexylmethyl) adipate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy) cyclohexane-meta-dioxane, and bis(2,3-epoxycyclopentyl)-ether, and optionally further comprising a polyol selected from polylactone polyols, polytetramethylene oxide polyols and polyalkylene oxide polyols, and/or further comprising a photoinitiator comprising a polyarylsulfonium salt.

18. A process of radiation curing a composition as defined in claim 15 wherein at least one of two conditions prevail, the first condition being that the amount of the photoinitiator present is less than that required to produce substantially the same cure rate in a corresponding composition not containing the cyclic ether, and the second condition being that the cure rate in the process is greater than that attainable in a corresponding composition not containing the cyclic ether.